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Multicomponent Diffusion Coatings,

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by L. S. Lyakhovich, L. G. Voroshnin, G. G. Panich, and E. D. Shcherbakov.

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In the book, the processes and results of simultaneous diffusion saturation of steels and alloys containing two or more elements have been examined; in most cases there is a formation of a diffusion layer on the metal surface of essentially higher quality as compared to multicomponent saturation layers. Extensive information is provided in relation to specific processes of simultaneous saturation of steels and alloys containing a wide range of elements such as boron, silicon, chromium and aluminum as well as in combinations of three elements. Advantages of mathematical modeling of the experiment in the study of thermochemical treatment have been indicated. The book is intended for scientists working on protective coatings on metals. It can also be of use to industrial scientists, graduates and post-graduates working in the field of metal physics. (Copyright (c) 1987 Oxonian Press Pvt. Ltd., New Delhi.)

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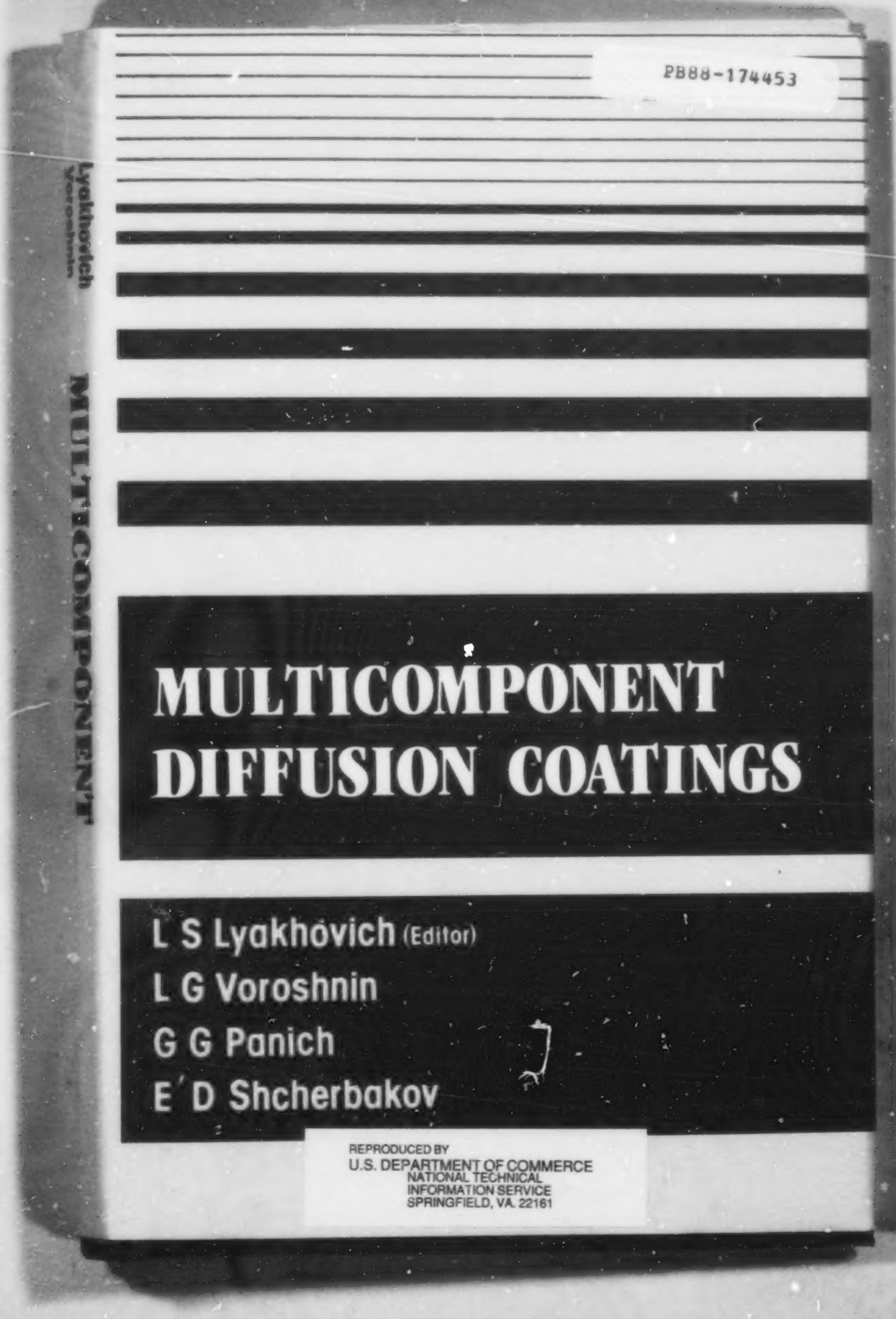

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Lyakhovich
Voroshnin
MULTICOMPONENT

MULTICOMPONENT DIFFUSION COATINGS

L S Lyakhovich (Editor)
L G Voroshnin
G G Panich
E D Shcherbakov

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[*Mnogokomponentnye Diffuzionnye Pokrytiya*]

L.S. Lyakhovich (Ed.), L.G. Voroshnin,
G.G. Panich and E'.D. Shcherbakov

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Introduction

Developments in chemical, electronic and other areas of industry, machine building, power engineering and nuclear technology and other branches of engineering technology impose stringent demands on the operational properties of materials as regards their resistance to wear, corrosion in liquid and gaseous media, cavitation erosion and many other types of external interactions.

Failure of components, instruments and other products in most cases originates from the surface and, in fact, the aforementioned requirements specifically relate to surface layers. Thus, in this respect, volume alloying of steels is, as a rule, uneconomical and in many cases not feasible, due to an almost total loss of ductility and toughness. Therefore, in recent years researchers and manufacturers have been paying greater attention to various techniques of surface hardening. Thermochemical treatment is one of the chief methods of surface alloying and, consequently, hardening.

Presently, processes of surface alloying of metals and alloys, such as carburizing, nitriding, aluminizing, etc., involving the use of a single element, are widely used. However, not many processes involving surface impregnation with three or more elements are available. There is, perhaps, only one such process used in industry, namely carbonitriding (i.e. cyniding).

It is obvious that surface alloying of a product with two or more elements provides a greater degree of flexibility in the properties of surface layers.

Only one monograph by Zemskov [1] and two books by Przhenosil [2] and Kriulin [3] have been published so far on multicomponent surface alloying.

As in one-component processes, multicomponent diffusion coating directly depends on the phase diagram of the system consisting of the substrate metal and various diffusing elements. Justification for the choice of this topic for investigation (apart for its practical application, as indicated earlier) is provided by the data of Petzov et al. [4]: considering that there are 80 'nonrare-earth' elements in the periodic table, the total number of systems, the phases of which have valuable properties, reaches the astronomical figure of 10^{27}. It appears that, on the basis of data available on the electron configuration of diffusing elements and the substrate metal and the corresponding binary phase diagrams (the available ternary diagrams are not well documented and cannot, therefore, be used for this purpose), quantitative predictions can be made in regard to the probable structural constituents that may be formed and the properties of multicomponent coatings produced by the diffusion processes.

In this work an attempt has been made to establish in the first approximation, correlation between the structure and properties of the base metal, the complex (multicomponent) source of the diffusing component and the resultant diffusion layer produced by their interaction.

PART ONE

Basic Principles of Multicomponent Diffusion in Metals

CHAPTER I

Certain Features of Multicomponent Diffusion

1. A GENERAL DESCRIPTION

There are three stages in any process involving thermochemical treatment:

1. *Formation of active atoms* in the medium which ensures the required alloying of the surface layer. Obviously, the number of active atoms formed per unit time will determine the strength of the diffusion source. The rate of formation of active atoms depends on many factors such as the state of aggregation and composition of the medium being used for diffusion saturation, the nature of interaction between the individual constituents of the medium among themselves and with that of the substrate, etc. These processes have been studied to some extent for one-component diffusion coatings and studies are being made for multicomponent diffusion processes.

2. *Adsorption* of active atoms being formed on the surface by the metal under treatment. The interactions between the surface of the metals (alloys) and elements or compounds, of ambient medium are complex and various aspects of these interactions are being investigated. However, it should be emphasized that the process of adsorption during thermochemical treatment resulting in subsequent diffusion of the adsorbed element in the volume has not been adequately studied. Information regarding the mechanism of formation of an adsorption layer which could be infused from the available data is very limited.

3. *Diffusion* of the elements in the volume of the metal (alloy): This process has been studied in greater detail. A large amount of literature is available on the qualitative and quantitative aspects of diffusion, self-diffusion and heterodiffusion. In recent years much attention has been paid to the study of the principles governing multicomponent diffusion saturation.

All these three stages of diffusion coating influence the kinetics of the thermochemical treatment, the microstructure and the constituent phases in the formed layer.

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The aforementioned principal stages of diffusion coating are closely related and it is often difficult to study their influences in isolation.

In the present work, the effect of interactions during the first and third stages on the resultant multicomponent diffusion saturation has been analyzed. As stated earlier, the information available on the intermediate stage (the second) is very limited, making it difficult to draw any general conclusions.

2. GENERAL PRINCIPLES GOVERNING THE FORMATION OF A STRUCTURE DURING MULTICOMPONENT DIFFUSION COATING

In the problem under investigation, it is of prime importance to systematize the possible combination of diffusing species which will enable prediction of the results of diffusion saturation.

On the basis of such a classification made by Arkharov et al. rests the nature of interaction between the diffusing species and the substrate [5, 6]. According to Arkharov, all combinations of the diffusing elements (during two-component diffusion saturation) can be subdivided into three categories:

1. Both the diffusing elements form compounds with the base metal and the pseudobinary system formed by these compounds indicates unlimited mutual solubility. As a result of diffusion saturation a single-phase coating is formed with a gradual variation in concentration of the diffusing species in the thickness of the layer.

The case of diffusion saturation of transition metals by two nonmetals belongs to the first category and can be extended to the Mo–C–N [7] system. The aforementioned version is often encountered in pseudobinary systems formed by intermetallic compounds.

2. Both the diffusing elements form compounds with the metal substrate. However, these compounds have a limited mutual solubility. A two-phase diffusion layer is formed; with the compound formed of the species with a higher coefficient of diffusion lying closer to the metal substrate. The distribution of the fast-diffusing species is exponential. According to the available data [5, 6, 8, 9], systems such as Cr–O–N, Cr–N–S, Cr–N–C belong to this category.

3. Both the diffusing elements form compounds with the base metal. However, they do not exhibit any mutual solubility. The diffusion layer consists of the compound of the base metal with that of the diffusing species which has a higher chemical affinity toward the base metal. The second element does not penetrate the base metal and no compound formation takes place, though under the given conditions it is thermodynamically quite stable. Systems such as Cr–O–S, W–C–N, Nb–B–C can be listed in this category [10, 12].

Unfortunately, [5, 6 and others] analysis has been limited only to combinations of those diffusing species which only form chemical compounds with the metal substrate.

A fairly large number of elements, which form among themselves pseudobinary systems (including their interaction with the substrate metal) such as a chemical compound—solid solution or solid solution I—solid solution II.

Most of the experimental work on diffusion saturation of metals and alloys with more than one element has been carried out at the Odessa Polytechnic Institute under the guidance of Zemskov [1, 13–23, etc.].

The classification of multicomponent diffusion saturation system according to Zemskov, is based on the nature of interaction between the diffusing species themselves. Various combinations of diffusing species (according to this classification) can be categorized in three groups.

1. The first group consists of elements which form (among themselves) solid solutions or intermetallic compounds over a wide range of compositional homogeneity. Solid solutions based on compounds of binary system of metal diffusing element or solid solutions of diffusing elements are formed in the diffusion layer. The zone of simultaneous diffusion of elements, where a change in structure is observed, shifts toward the species which has a lower rate of diffusion. The thickness of the diffusion coating gradually increases with an increase in the concentration of the fast-diffusing element in the active mixture. There are no maximal or minimal points on the plot of composition of the mixture versus thickness of the diffusion layer. According to some authors [13] Al–Si, Cr–Al, Cr–Si, Ti–Al, Ti–Si, Cr–Ti, systems belong to this group.

2. The second group consists of those impregnating elements which exhibit very little mutual solubility at the process temperature, but form chemical compounds. At specific compositions, there exists a clear minimum on the plot of composition of the mixture versus thickness of the diffusion layer. In the diffusing mixture, the diffusing elements form compounds among themselves. According to authors of [13], systems such as B–Al, B–Si, B–Ti, Cr–Zr, B–Mn and Al–Ce belong to this group.

3. The third group comprises elements which do not form solid solutions but form stable chemical compounds over a very narrow range of compositional homogeneity. At a certain composition of the mixture, in this case, a diffusion layer is either completely absent or is of a negligible thickness. Systems such as B–Cr and B–Ce belong to this group.

It is obvious that the difference between the second and third categories is not significant and is somewhat qualitative in nature.

The occurrence of a minimum on the plot of composition of the mixture versus thickness of the formed diffusion layer is explained [13] by the formation of stable compounds by diffusing elements with the base metal. The position of the minimum in regard to thickness of the diffusion layer is related to the point on the phase diagram corresponding to the stoichiometric composition of the chemical compounds.

In the Ti–Al and Ti–Si diffusing systems, stable chemical compounds of fixed compositional homogeneity may be formed, and these belong either to the 2nd or the 3rd group. In the B–Al and B–Si systems, however, no chemical compound is normally formed at diffusion temperatures and these are included in the 1st group. Despite the foregoing inconsistencies, Zemskov's classification deserves due consideration.

The very existence of these two classifications justifies consideration of the nature of interaction between diffusing species among themselves in the active mixture and also between individual diffusing species with the substrate metal for predicting the results of multicomponent diffusion operations. In other words, the chemical affinity of all the components forming the diffusion coating influences the results of multicomponent diffusion coating. To assert the correctness of this statement, the following example may be considered: The results of diffusion saturation of iron, mild steel and ZhS6K alloy simultaneously with boron and titanium have already been given [13, 24]. It is important to note that the location of the minimum of the thickness of the diffusion coating depends on the nature of material being diffusion coated. Such a situation would not arise if the results of diffusion saturation were dependent only on the interaction between the diffusing species in the active mixture.

Results of multicomponent diffusion saturation can be better represented by the plot of composition of the mixture versus the thickness of the diffusion layer (to be more precise, it should be described as a plot of mixture composition–layer thickness–phase composition). In this case they contain more useful and detailed information in regard to the results of diffusion saturation.

From analysis of the data given in [1, 13–23, 325, etc.], it can be concluded that, in addition to the chemical affinity of the elements, the potential of the diffusion source, the diffusivity of the elements and the concentration dependence of the coefficient of diffusion also influence the results (i.e. mixture phase diagram–layer thickness–phase composition plot). The necessity for considering these factors can be better understood from the following examples. In systems such as Zr–Si, Zr–Al and Ti–Si, stable compounds of fixed compositions or of a limited range of compositions exist at the impregnation temperature. However, there are no extremal points on the plot of mixture composition versus thickness of the diffusion layer. On the other hand, in systems such as B–Al, B–Si and especially in Si–Al and Mo–W, there is no chemical-compound formation in the active mixture at the process temperature. However, under certain conditions of diffusion saturation, there does exist a well-defined minimum on the plot of composition of the mixture versus thickness of the diffusion layer.

From the analysis of the results of [1, 5, 6, 13–23, etc.] it can be further concluded that the phase diagram of the diffusion layer is mostly determined by the chemical affinity of the elements and the potential of the diffusion source with respect to each of the diffusants. However, the shape of the plot of composition of the mixture versus thickness of the diffusion layer and the absolute values of the resultant diffusion coating also depend on the diffusivity or the diffusing elements and the concentration dependence of the coefficient of diffusion.

An attempt has been made below to generalize the information available in the literature and the results of our own investigations on equilibrium diagrams of composition of mixture, the depth of the layer and phase composition of the layer.

Various methods of diffusion saturation were employed to obtain alloyed coatings: impregnation using fine powders of pure elements with and without activators (vapor-phase and gas-phase contact methods, according to the classification of Dubinin), impregnation using powdered oxides (aluminothermic method) and impregnation using fused baths (electrolytic and electroless versions).

3. EFFECT OF CHEMICAL AFFINITY OF ELEMENTS ON MULTICOMPONENT DIFFUSION SATURATION

The ternary systems (of two diffusants and one substrate) involved in the process of diffusion-layer formation can be subdivided into four basic groups, depending upon the nature of interaction between the components.

Systems of type I—These are the systems in which one of the diffusing species forms compounds of fixed composition (to be precise—with a very narrow region of homogeneity) with the other diffusant as well as with the base metal. To this group belong those systems in which one of the diffusing species is a covalent nonmetal of low atomic number (C, N, B, Si) (the basis of strong metallic compound, preferably with covalent metallic bonds) and the other being a transition metal, with significantly unoccupied *d* orbitals. In such cases metallic compounds of practically fixed composition are formed in the active mixture.

The diffusion layer consists of the same phases which are formed during diffusion saturation with the individual diffusants. Their distribution along the depth of the diffusion layer is similar to the distribution during one-component diffusion saturation from a diffusion source of identical chemical potential. The concentration of the second element in the diffusion layer does not exceed its solubility limit in the corresponding phases of the diffusion layer. This determines its distribution along the depth of the coating. Interaction of the elements in the impregnating mixture affects the results of diffusion saturation by a variation in the chemical potential of the diffusion source for each diffusant. The chemical potential of the diffusion source varies in such a case not only due to the change in composition of the mixture but also due to the formation of stable chemical compounds in it. The mixture composition versus depth of layer phase diagrams reveal discontinuities or sharply expressed minima with respect to the depth of layer.

As regards the diffusion saturation of iron the following systems can be listed into a group: Cr–B, Mo–B, W–B, Ti–B, Cr–C, Mo–Si, W–Si, Mo–C, W–C, Nb–B, Nb–C, Zr–C and other similar combinations.

Some experimental data related to these systems is considered below:

Simultaneous diffusion saturation of boron in steel using a melt of borax and chromium oxide was carried out by the electrolytic method. When the Cr_2O_3 content in the melt was less than 5% only boriding took place. With 8–10% of Cr_2O_3 the diffusion layer was almost nonexistent, and at still higher concentrations of chromium oxide, chromizing took place. Chromium boride was detected in the impregnating mixture. Similar results have been reported for simultaneous boriding and chromizing using powders of pure metals [325].

An attempt to obtain a two-component diffusion coating with boron and molybdenum (or tungsten) did not also yield successful results [323]. In this case either boriding of molybdenizing (or tungstenizing) took place while, in a certain composition range of the melt there was no diffusion-layer formation.

Simultaneous diffusion saturation of steel with silicon and active silicide formers such as Mo and W was investigated by the electrolytic impregnation method [323]. For molybdeno- and tungsteno-siliciding melts of sodium silicate with additions of sodium molybdate and sodium tungstate respectively, were used. Results of molybdeno-siliciding are shown in Fig. 1.

Siliciding was observed only when molybdate was completely absent in the bath. When the Na_2MoO_4 content was 5%, the diffusion layer on medium carbon steel was absent; on Armco iron a layer of α-phase with a reduced thickness was formed (as the result of a fall in the potential of the diffusion source of silicon and a simultaneous diffusion of silicon and molybdenum in the solid solution). In all other melts a preferred molybdenizing took place on Armco iron, the layer being of α-phase and, on steel 45, it consisted of the carbide, Mo_2C. Similar results were obtained in the case of simultaneous diffusion saturation with silicon and tungsten. Examples of a similar type are further listed in [24, 134, etc.].

Since all the low atomic number nonmetals listed above are highly active chemically, there cannot be any doubt about their interaction with the second component in the active impregnating mixture and the resultant reduction in the thickness of the diffusion layer. However, such an approach to explain the experimental data appears to be oversimplified. Formation of a chemical compound in the mixture should not lead to sharp reduction in layer thick-

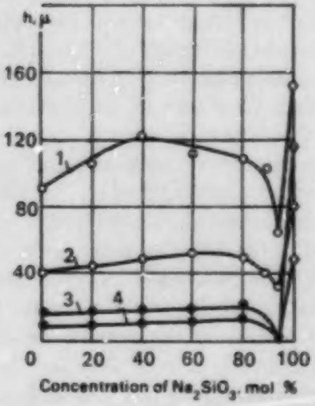

Fig. 1. Simultaneous diffusion saturation of iron and steel with molybdenum and silicon using an electrolytic method at a current density of 0.25 A/cm^2:

1 and 2—Armco iron; 3 and 4—Steel 45; 1 and 3—1100°C; 2 and 4—950°C.

ness in a very narrow range of composition of the active mixture (as chemical compounds are formed in practically the entire composition range of the impregnating mixture, except in pure metals) or appear to be the reason for complete absence of the layer, as a fairly large number of cases are known where stable chemical compounds are used as diffusion sources [25–32]. The situation is possibly, aggravated by the nature of interaction of the diffusants with the base metal (the interaction with the phases formed in the diffusion layer).

Let us examine this aspect in the case of borochromizing. During surface impregnation using active mixtures rich in boron, a borided layer is formed on iron. Chromium has no appreciable solubility in borides of iron [33]. Therefore, all the chromium powder not reacting with boron remains passive during the formation of a diffusion layer (alloying of iron boride with chromium does take place but it does not change the general line of reasoning) and plays the role of an inactive addition. A similar situation arises during diffusion saturation of steel in mixtures rich in chromium: boron is practically insoluble in carbides of chromium.

Thus, the second element remains almost passive during the formation of the diffusion layer.

The overall effect of the aforementioned factors (formation of compounds in the mixture and interaction between the phases formed) leads to the results reported.

Systems of type II—These are systems in which diffusing species form chemical compounds among themselves as well as with the base metal, preferentially forming metallic bonds. They are less stable as compared to the compounds in systems of the first group, and as a rule, have a wide range of composition. They influence the results of impregnation in a manner similar to compounds of impregnating elements of the first group (reduce the chemical potential of the diffusion source and, consequently, the thickness of the diffusion layer), albeit with lesser severity.

Generally the diffusion layer is a solid solution of diffusing species with the base metal or a chemical compound of one of the diffusing species with the base metal. However, formation of a two-phase layer cannot be ruled out (at a very high potential of the diffusion source). In such a case the chemical compound of the fast-diffusing species is formed at the advancing front. The distribution of the diffusing species in the diffusion layer is of an extremal nature. The plots of composition of the mixtures versus depth of the diffusion layer are either without a clearly defined minimum or are devoid of it. The latter is characteristic of systems in which there is practically no chemical reaction and one of the diffusing species has a much higher diffusion mobility as compared to the other (systems Mo–Al, W–Al and Cr–Al, etc.).

In case of impregnation of iron, the following systems are placed in the second category—Cr–Ti, Cr–Al, Ni–Al, Mn–Al, Nb–Al, V–Al and other intermetallic systems.

Results of diffusion coating with elements of the second group can be conveniently analyzed using aluminide systems as an example. Characteristic diagrams of systems of this group are given in Fig. 2. Qualitatively, the results of vanadium–aluminum, titanium–aluminum and chromium–aluminum diffusion saturation are similar. At higher concentrations of transition-element oxides in the active mixture the layer formed is the corresponding carbide (on a high-carbon steel base) or a complex α-solid solution (on iron).

When the content of oxide is moderate, a two-component diffusion saturation is observed which, depending on the ratio of the diffusivities of the transition element and aluminum, may be accompanied by an increase or decrease in ferrite-layer thickness. At higher concentrations of aluminum in the active mixture 'pure' aluminizing takes place. Similar results were obtained for systems such as: Mo–Al, Zr–Al, Cr–Si, Cr–Ti. The absence of extremal points in the plots (Fig. 2, b) is probably related, not to any specific characteristic of interaction between diffusants but, to the marginal effect of limiting the thickness of the layer and a rather crude experimental method. In other words, the nature of the plot of composition of the mixture versus thickness of the diffusion layer is same for systems of the second group, as observed for systems of the first group. However, the effect of a reduction in thickness of the diffusion layer in the latter case is hardly apparent.

Systems of type III—Diffusing species and the base metal form a complex solid solution in a ternary system. The diffusion layer consists of a multicomponent solid solution with the substrate metal as a parent phase.

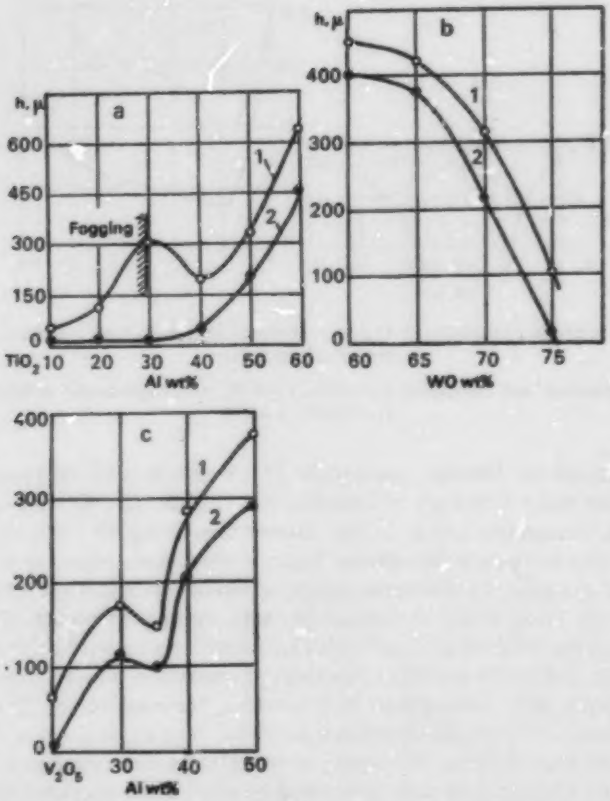

Fig. 2. Simultaneous diffusion saturation of plain carbon steels with a) titanium and aluminum, b) tungsten and aluminum and c) vanadium and aluminum by aluminothermic method ($t=1100°C$, $\tau=4$ h, 30% Al_2O_3, 5% AlF_3, 2% NH_4Cl):

1—Armco iron; 2—Steel U8.

It is stipulated that of all diverse types of the aforementioned systems only those with a significant intersolubility of elements are included in this group. For diffusion saturation of iron, the following systems can be listed in this category: Cr–Mo, W–V, Mo–W, V–Mo, Cr–Ti, Cr–Mn, Co–Ni, Ni–Pt, Co–Pd, Pt–Ir, etc.

Simultaneous diffusion saturation of iron with chromium and manganese (Fig. 3, a) and tungsten and molybdenum (Fig. 3, b) are good illustrations of this type of interaction.

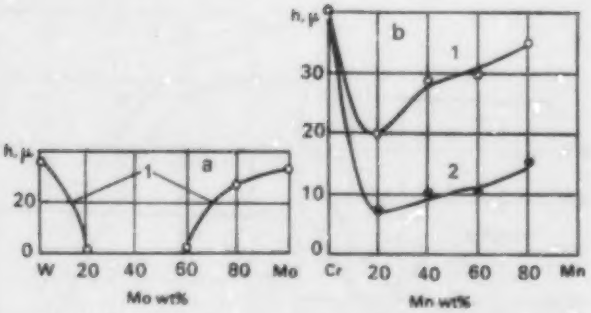

Fig. 3. Diffusion saturation of 1) Armco iron and 2) steel 45 with combinations of elements of type III

a—Chromium and manganese ($t=950°C$, $\tau=4$ h); b—Tungsten and molybdenum ($t=1050°C$, $\tau=6$ h).

Simultaneous diffusion saturation of chromium and manganese was carried out using a mixture of ferrochromium (grade 75% Cr) and commercial-grade manganese metal. In the mixture containing 40–100% of manganese, a predominantly manganese impregnation takes place, at a 10–40% manganese content simultaneous impregnation of chromium and manganese and, at still lower levels of manganese, only chromizing occurs. On steels, along with the solid solution, a carbide zone forms on the surface; in mixtures rich in chromium this consists of carbides of chromium alloyed with manganese and iron and, in manganese-rich mixtures, there are cementite-type carbides, Mn_3C, alloyed with chromium and iron. The curve given in Fig. 3, a depicts the basic features of systems of type III. In the central part, the diagram has a floating minimum determined by a fall in the potential of the diffusion source with respect to each of the components and, possibly, by the concentration dependence of their coefficients of diffusion.

In the case of simultaneous diffusion saturation of tungsten and molybdenum there is a discontinuity in the plot of composition of the mixture versus thickness of the layer for an intermediate range of composition of the impregnating mixture (from 20 to 60% Mo). As no other contradictory data on simultaneous diffusion of these elements in iron is given in the literature, the observed phenomenon can only be explained by assuming that, in this concentration range, the quantities of the diffusing species (W and Mo) entering from the mixture are not sufficient to extend beyond the γ-region of iron.

Systems of type IV—Species which cannot interact among themselves in the active mixture belong to this system. The results of diffusion saturation are determined entirely by the nature of interaction between the diffusing species and the substrate metal. The following combinations of diffusing species fall in this category: C–N, B–C, B–Al, B–Si, B–Cu, Al–Si, Cu–C and similar systems.

In the case of formation of compounds of the diffusing species and substrate metal, the nature of such interaction conforms to the principles discussed by Arkharov [5, 6].

In the case of formation of a solid solution by diffusing species with the base metal, the results of diffusion saturation are similar to those discussed earlier (see—Systems of type III). Therefore, while discussing the results of 'Systems of type IV' only more interesting examples have been considered. (Along with these, to some extent, interactions other than those mentioned above are also included.)

1. Impregnating elements in the mixture do not interact and form separate phases in the diffusion layer. Mainly combinations of nonmetals with low atomic numbers (boron, nitrogen, carbon) and nonmetals with high atomic numbers, forming substitutional solutions in the layer, are given as examples of this type. Though a large number of such examples can be found, the discussion here is limited to the most glaring example of combinations of boron with α-stabilizers (aluminum and silicon), however, it should not be presumed that the components of Al–B and Si–B systems cannot interact with each other as the existence of borides of aluminum and silicides of boron is well established. However, their formation takes place under certain specific conditions which are not satisfied during thermochemical processing, for instance, at temperatures above the melting point of iron. Experiments by different investigators on these processes (which have been extensively studied) show that compound formation in B–Al and B–Si systems, either in salts or in active mixtures, is not possible.

Results of boroaluminizing of iron and steel U8 by aluminothermic methods are shown in Fig. 4, (a). Boronizing takes place in a mixture containing up to 40% of Al. The thickness of the layer increases with a rise in the chemical potential of the diffusion source (95% corresponds to the quantity of aluminum necessary for complete reduction of boric anhydride). At 60% of aluminum, a practically pure aluminizing takes place. In the concentration range of 35–60% of aluminum, a simultaneous diffusion saturation of boron and aluminum takes place. It can be seen that these results agree with the data given in [271] (Fig. 4, b). The plots of composition of the mixture versus thickness of the diffusion layer are typical for boroaluminizing and for other systems of this type under consideration.

Results of borosiliconizing of iron and steel by a gas-phase and electroless liquid method are given in Fig. 4, (c) and (d). These are similar to the results given earlier for other cases and a further explanation is not necessary.

The diffusion layer formed by combined impregnation of boron and aluminum (or silicon) consists of the phases formed by both the elements;

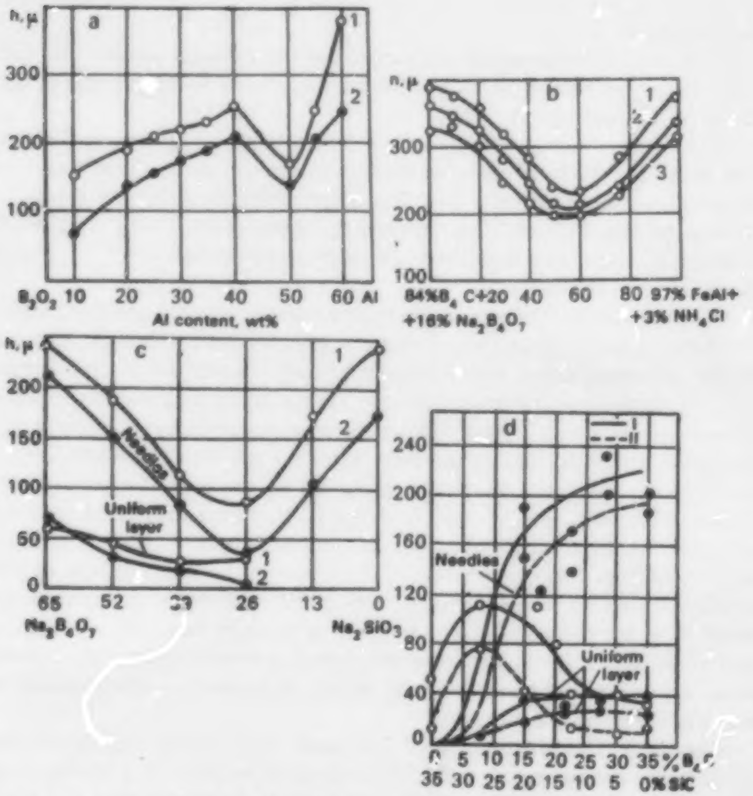

Fig. 4. Boroaluminizing (a, b) and borosiliconizing (c) of (a) Armco iron, (2) steel 45 and (3) steel U8:

a—Aluminothermic diffusion coating in mixture—$B_2O_3 + Al + 70\%\ Al_2O_3 + 0.5\%$ sodium fluoride ($t = 1100°C$, $\tau = 4$ h); b—Diffusion coating in a gaseous medium ($t = 1050°C$, $\tau = 6$ h); c—Nonelectrolytic liquid impregnation ($t = 1025°C$, $\tau = 6$ h) borax + sodium monosilicate + 35% silicon carbide; d—Reduction of monosilicate (65%) with a mixture of carbides B_4C and SiC.

(I—boronizing; II—siliconizing).

naturally, the fractions of these phases are proportional to the concentrations of the respective elements in the impregnation mixture.

Thus, the characteristic of systems of this type is that the diffusivities of the impregnating elements in the layer are independent of each other. (Diffusion saturation of elements is independent of each other.) One of them, generally, forms a stable compound of fixed composition and the other forms a solid solution with the substrate metal, the solid solution being permeable to diffusion of the first element. If the diffusion source for the first species is stronger than that of the second, diffusion of the latter may be completely suppressed. In an opposite case simultaneous diffusion takes place with the formation of a mixture of the mentioned phases. The degree of dispersion and spatial distribution of the constituent phases in the diffusion layer can be widely varied. They depend on such a large number of variables that it is practically impossible to predict them. Therefore, to obtain a diffusion coating with a combination of only the desirable properties of both the individual phases without any of their drawbacks appears to be difficult.

2. These systems are characterized by two impregnating elements in the mixture with no interaction between them but, unlike in the earlier case, with no independence in regard to diffusion in the layer.

Simultaneous diffusion coating of steel with aluminum and silicon is an example of this type. Results of aluminosiliciding by the gas-phase impregnation method are given in Fig. 5, (a). As a result of diffusion saturation stable ferrite is formed. The thickness of the ferrite layer gradually reduces with the replacement of aluminum by the more mobile silicon in respect of its diffusion properties.

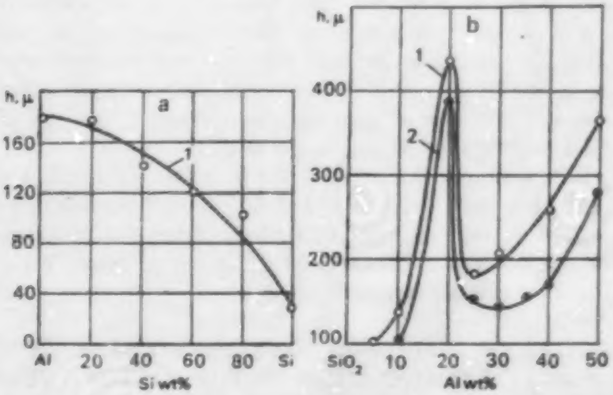

Fig. 5. Diffusion coating of 1) Armco iron and 2) steel 45 with elements of the fourth type—aluminum and silicon:

a—Impregnation from powder of elements ($t=1050$°C, $\tau=6$ h, 50% Al_2O_3); b—Aluminothermic impregnation ($t=1000$°C, $\tau=4$ h, 60% Al_2O_3, 2% sodium fluoride).

The simple nature of the plot of composition of the mixture versus thickness of the diffusion layer is retained during aluminosiliconizing of steel, but only till the activities of aluminum and silicon are not high enough to form the superlattice structures, Fe_3Si and Fe_3Al. The rate of formation of the superlattice layer is significantly higher than that of stable ferrite and the mutual solubility of these superlattice phases is fairly limited. Therefore, the plot of the process changes to the form shown in Fig. 5 (b), at low concentrations of silicon. Pure aluminizing takes place with the formation of Fe_3Al layer and α-phase. With a decrease in the aluminum content in the mixture the depth of the aluminized layer is, naturally, reduced. The amount of SiO_2 is then sufficient for siliconizing to take place whereupon, due to the higher concentration of the reducing agent (aluminum), a deep layer of α-phase of Fe_3Si is formed (also containing, probably, some percentage of aluminum). With a decrease in the quantity of the reducing agent the process of diffusion saturation gradually slows down (the superlattice structure in the layer is replaced by a solid solution of silicon in ferrite).

The cases analyzed here supplement the clarification of Arkharov and the inclusion of the results given above (see 'Systems of type III') renders this classification fairly complete.

The classification of two-component diffusion saturation proposed above is not claimed to be final and ideal. However, with the information available on the technology of impregnation, it enables a qualitative prediction of the structural constituents of the diffusion layer formed and, to a certain extent, can provide a logical prediction with regard to its properties. Thus, for example, it is obvious that multiphase diffusion layers are not suitable for forming corrosion-resistant coatings. For obtaining wear-resistant coatings preference should be given to diffusion layers containing intermetallic compounds (Ist and IVth type of systems), the IInd and IIIrd types of systems being most promising for heat-resistant coatings.

It has been mentioned earlier that the potential of the diffusion source and concentration dependence of the diffusion coefficients of the diffusing elements have a strong influence on the shape of the plot of composition of the active mixture versus thickness of the diffusion layer. We shall now analyze the effect of these factors in detail.

4. POTENTIAL OF DIFFUSION SOURCE AND BASIC TYPES OF THE PLOTS OF COMPOSITION OF THE MIXTURE VERSUS THICKNESS OF THE DIFFUSION LAYER

In the case of one-component diffusion saturation it is convenient to assume that the depth of the diffusion layer is limited by the process of diffusion in the metal being processed. However, according to current understanding, the potential of the diffusion source situated outside the surface of the metal being diffusion coated plays a very important role in obtaining the required results.

It should be remembered that a 100% concentration of the diffusing element available in the vicinity of the surface of the component does not imply the highest limit of the potential of the source as, in fact, the concentration of the active element capable of diffusing is always significantly low [35]. For example, during investigations on boriding in a melt of borax and boron carbide, it has been established that the quantity of boron contained in the bath was theoretically sufficient for continuous processing for a few thousand hours. However, conversion of all the boron from the melt to boride of iron could not be achieved in practice. At the moment of the so-called depletion of the bath, the total quantity of the diffusing element drawn in the form of borides constituted less than 1% of the total quantity. It can be easily seen that the higher the difference between the 'theoretical absolute' and practically extractable quantities of the diffusing species, the lesser the capacity of the impregnating medium to complete the corresponding process of formation of the diffusing species.

Thus, presently the potential capacities of active mediums are used to a very limited extent. Apparently, for their complete exploitation, it is necessary, in each case, to conduct a very careful study of the mechanisms of chemical and electrochemical processes taking place on an impregnating medium. If hitherto this has not been done with the required thoroughness, the reason can be the following: to most of the specialists on diffusion coating it appeared obvious that an increase in the potential of an external diffusion source does not play any important role. It was considered axiomatic that since the slowest step in diffusion saturation is the diffusion of the impregnating element in the existing layer the diffusion source cannot be so weak that the process of diffusion might overtake it, i.e. the diffusing species is resorped in the metal at a faster rate than it is formed in the source [36]. At the same time it can be implied that the concentration of the diffusing species on the surface from where solid-phase diffusion begins, is constant, although it can be understood from the earlier statement that the diffusion process being slower, the diffusing species should accumulate at the surface of the metal [37, 38]. This has been mathematically represented in [39]. It has been shown that the quantity of material transported by the active medium to the surface of the specimen is directly proportional to the difference between the equilibrium concentration of the 'upper' phase of the layer (i.e. concentration, corresponding to this phase, according to the phase diagram), temperature and the actual concentration in the surface layer at a given moment C_s:

$$\frac{dM}{d\tau}=k\,(C^0-C_s),$$

where k is a kinetic coefficient.

The exact strength or potential of the diffusion source can be known from the concentration of the diffusing element in the surface films in contact with the active medium (to be precise, in contact with the sorption layer). This concentration can be measured and its variation characterizing the potential of the diffusion source can be calculated. Moreover, this surface layer itself can be regarded as the diffusion source. In [40], this variation has been investigated for high-temperature vacuum chromizing. The following correlation has been obtained

$$C_\tau - Z_0 = a\,(\tau - \tau_0)^{1/4},$$

where Z_0 is the initial concentration of the impregnating element in the metal: τ_0 is the incubation period for diffusion saturation with the α-stabilizing element—the duration of short-circuiting of the γ-field and, a is the constant of proportionality. The correlation is of the form of a damping parabola.

Similar data is available on theoretical work [41]. During chromizing at high temperatures in a gaseous medium the exponent in the aforementioned equation becomes equal to one, i.e. the dependence is linear [42]. However, the authors of this work point out that it is characteristic only for very favorable conditions of diffusion saturation (for example, for high-temperature processes). This function should be linear even when increasingly concentrated compounds are formed on the surface of the layer. The graph of function $C_\tau = f(\tau)$ will almost resemble horizontal 'steps' corresponding to increasingly saturated phases with no fixed ranges of composition.

A reduction in the potential of the diffusion source with time, according to [43, 44], takes place in the following cases:

a) the simplest case: potential of the source remains constant $C_\tau - Z_0 = a =$ const. The source is either a liquid or a gaseous phase with an infinitely large volume as compared to the volume of the object or is a compound of fixed composition. In the latter case the interface should move with time towards the source phase;

b) the potential of the source decreases with time in a parabolic manner

$$C_\tau - Z_0 = a\left(\frac{\tau - \tau_0}{t}\right)^{\tau/2},$$

where τ_0 is the incubation period for layer formation, and t the temperature of the process (const). This relationship is applicable if the source is a solid solution at the interface between the source and the phase under consideration and there is an abrupt change in concentration. The entry of the alloying element is limited by the process of diffusion across the phase-source interface;

c) the potential of the source falls linearly with time

$$C_\tau - Z_0 = a\left(\frac{\tau - \tau_0}{t}\right).$$

The decrease may be due to a fall in concentration of the impregnating element in the active medium (for example, during the use of a powder mixture without an activator).

Thus, in practice, widely diversified relationship for variation in the potential of the diffusion source with time are encountered. If there is any doubt about the progressive character of this dependence (for example, during resorption of an already existing layer, or diffusion saturation in a medium with very low activity) then, while determining the duration of the process, it is necessary to take into account the decrease in potential according to one of the relationships given above.

It has been repeatedly pointed out that the potential of the diffusion source has a decisive influence on the type of the plot of composition of the mixture versus thickness of the diffusion layer and, consequently, on the results of two-component diffusion saturation. These phenomena are discussed below for pure diffusion, i.e. without considering the interaction between the diffusing species in the active mixture and neglecting the interaction between the diffusion fluxes in the specimen. Classification of the basic types of plots of composition of the mixture versus thickness of the diffusion layer based on general principles of thermodynamics will also be discussed.

To start with, diffusion of a single element accompanied by a phase transformation will be considered (Fig. 6, a). As stated earlier, interaction between diffusion fluxes will not be considered, i.e. the coefficients of cross diffusion are not taken into account in the following expressions:

$$I_1 = -D_{11}\frac{\partial C_1}{\partial x} - D_{12}\frac{\partial C_2}{\partial x},$$

$$I_2 = -D_{21}\frac{\partial C_1}{\partial x} - D_{22}\frac{\partial C_2}{\partial x}, \tag{1}$$

as efforts are concentrated on determining the boundary concentration of the diffusing elements. The interface moves according to the following relation

$$x_1 = \xi_0\sqrt{t}, \tag{2}$$

where ξ_0 is found from the solution of Eq. (2) (see, for example, [34]);

$$\sqrt{\frac{D_1}{\pi}}\cdot\frac{C_s - C_1}{\Phi(\xi_0/2\sqrt{D_1})}\,e^{-\frac{\xi_0^2}{4D_1}} - \sqrt{\frac{D_2}{\pi}}\times\frac{C_2}{1-\Phi(\xi_0/2\sqrt{D_2})}\,e^{-\frac{\xi_0^2}{4D_2}} = \frac{C_1 - C_2}{2}\,\xi_0;$$

$$\Phi(\omega) = \frac{2}{\sqrt{\pi}}\int_0^{\omega} e^{-\omega^2}\,d\omega \text{—error function.}$$

We will conduct a comprehensive analysis of the variation in quantity ξ_0 with the interfacial concentration C_s.

When C_s is close to C_1, ξ_0 is small. For small values of ξ_0

$$\Phi\left(\frac{\xi_0}{2\sqrt{D_1}}\right) \approx \frac{\xi_0}{\sqrt{\pi D_1}}. \tag{3}$$

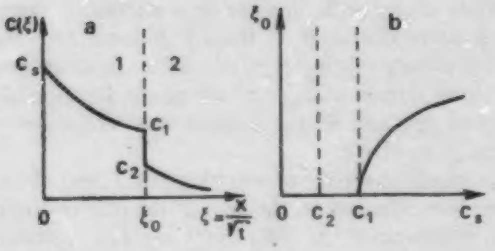

Fig. 6. a) Concentration variation of diffusing element during its transport through the interface of the first type and b) variation of ξ_0 with the interfacial concentration of the diffusing species C_s.

Substitution of (3) in (2) gives,

$$\xi_0 \approx \frac{C_s - C_1}{C_2}\sqrt{\frac{\pi D_1^2}{D_2}}, \quad \frac{C_s - C_1}{C_2} \ll 1. \tag{4}$$

For higher values of C_s, ξ_0 is large. In such a case

$$\Phi\left(\frac{\xi_0}{2D_1}\right) \approx 1 - \frac{2}{\xi_0}\sqrt{\frac{D_1}{\pi}}\, e^{-\frac{\xi_0^2}{4D_1}}. \tag{5}$$

Thus,

$$\xi_0 \approx 2\lambda\sqrt{D_1}, \qquad \frac{C_s - C_1}{C_1} \gg 1, \tag{6}$$

where λ is determined from the equation

$$\frac{C_s - C_1}{C_1} = \sqrt{\pi}\lambda\, e^{\lambda^2}. \tag{7}$$

It is easily seen that:

$$\lambda \approx \left(\ln\frac{C_s - C_1}{C_1\sqrt{\pi}} - \frac{1}{2}\ln\frac{C_s - C_1}{C_1\sqrt{\pi}}\right)^{1/2}. \tag{8}$$

On the basis of the correlations obtained above (Eqs. (4), (6) and (8), the nature of variation of ξ_0 with the boundary concentration C_s is shown in Fig. 6 (b).

We will now consider two-component diffusion. Leaving aside the mechanism of formation, supply and adsorption of active atoms of the impregnating element on the suface being impregnated, we will consider the conditions of equilibrium at the interface of the adsorption layer and the substrate metal which very quickly leads to diffusion coating. The adsorption layer on the surface being impregnated consists of only adsorbed atoms of elements *A* and *B*, i.e. a binary system. Thus, the conditions of equilibrium of chemical potentials of these elements in the adsorption layer and the substrate metal are represented as follows:

$$\begin{cases} \mu_A^a(C_A^a)=\mu_A(C_A, C_B), \quad \mu_B^a(C_B^a)=\mu_B(C_A, C_B), \\ C_A^a+C_B^a)=1. \end{cases} \tag{9}$$

The superscript *a* corresponds to quantities in the adsorption layer. For the sake of brevity, pressure and temperature terms in Eq. (9) have not been given. Concentrations C_A and C_B correspond to the concentration of elements *A* and *B* in the specimen being impregnated.*

By means of Eq. (9), let us analyze how an increase in the concentration of component *B* in the mixture ($\delta C_B^0>0$) affects the interfacial concentrations C_A and C_B. Obviously, the variation in concentration of adsorbed atoms *A* and *B* is related with δC_B^0 as follows:

$$\delta C_B^a=f\delta C_B^0, \quad \delta C_A^a=-f\delta C_B^0. \tag{10}$$

The value of *f* depends on the composition of the mixture and conditions of diffusion saturation. Practically, the factor *f* is always positive although under certain conditions of impregnation it may become negative.

From Eqs. (9) and (10) we obtain,

$$\begin{aligned} -\frac{\partial\mu_A^a}{\partial C_A^a} f\delta C_B^0 &= \frac{\partial\mu_A}{\partial C_A}\delta C_A+\frac{\partial\mu_A}{\partial C_B}\delta C_B, \\ \frac{\partial\mu_B^a}{\partial C_B^a} f\delta C_B^0 &= \frac{\partial\mu_B}{\partial C_a}\delta C_A+\frac{\partial\mu_B}{\partial C_B}\delta C_B. \end{aligned} \tag{11}$$

Here the dependence of μ_A^a and μ_B^a on the surface concentration of adsorbed atoms has been neglected. This is permissible because, in the process of diffusion, the impregnation surface concentration of adsorbed species reaches levels close to the limiting values corresponding to the formation of a monomolecular film.

Variations in boundary concentration δC_A and δC_B due to increase in the concentration of element *B* in the mixture, according to Eq. (11) can be expressed as follows:

$$\delta C_A=\frac{D(C_A, C_B)}{D(\mu_A, \mu_B)}\left(-\frac{\partial\mu_B}{\partial C_B}\cdot\frac{\partial\mu_A^a}{\partial C_A^a}-\frac{\partial\mu_A}{\partial C_B}\cdot\frac{\partial\mu_B^a}{\partial C_B^a}\right)f\delta C_B^0, \tag{12}$$

$$\delta C_B=\frac{D(C_A, C_B)}{D(\mu_A, \mu_B)}\left(\frac{\partial\mu_A}{\partial C_A}\cdot\frac{\partial\mu_B^a}{\partial C_B^a}+\frac{\partial\mu_B}{\partial C_A}\cdot\frac{\partial\mu_A^a}{\partial C_A^a}\right)f\delta C_B^0, \tag{13}$$

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*For the sake of brevity the lower index of quantities C_A and C_B has been dropped.

where

$$\frac{D(C_A, C_B)}{D(\mu_A, \mu_B)} = \begin{vmatrix} \frac{\partial \mu_A}{\partial C_A} \cdot \frac{\partial \mu_A}{\partial C_B} \\ \frac{\partial \mu_B}{\partial C_A} \cdot \frac{\partial \mu_B}{\partial C_B} \end{vmatrix}. \tag{14}$$

The thermodynamic inequality in this case is (see [34]):

$$\frac{D(\mu_A, \mu_B)}{D(C_A, C_B)} > 0; \quad \frac{\partial \mu_A}{\partial C_A}, \ \frac{\partial \mu_B}{\partial C_B}, \ \frac{\partial \mu_A^e}{\partial C_A^e}, \ \frac{\partial \mu_B^e}{\partial C_B^e} > 0. \tag{15}$$

From correlations (12) and (13), it can be seen that if $d\mu_A/dC_B > 0$, then $\delta C_A < 0$, $\delta C_B > 0$*. This corresponds to a situation in which an increase in the concentration of element B raises the activity of element A, i.e. it reduces its solubility. If $d\mu_A/dC_B < 0$ (i.e. B reduces the activity of A) there is a possibility of $\delta C_A > 0$. The following condition should then be fulfilled (see [12]):

$$-\frac{\partial \mu_A}{\partial C_B} \cdot \frac{\partial \mu_B^e}{\partial C_B^e} > \frac{\partial \mu_B}{\partial C_B} \cdot \frac{\partial \mu_A^e}{\partial C_A^e}. \tag{16}$$

For an exhaustive analysis of this inequality (16), in place of μ_A^e, μ_B^e and μ_B we will use the expression for chemical potential in dilute solutions:

$$\begin{cases} \mu_A^e = RT \ln C_A^e + \psi_A^e, \ \mu_B^e = \mu_{B,0}^e - RT\,C_A^e \\ \mu_B = RT \ln C_B + \psi_B. \end{cases} \tag{17}$$

Substituting (17) in (16), and consideration that

$$\frac{\partial \mu_A}{\partial C_B} = \frac{\partial \mu_B}{\partial C_A},$$

the inequality (16) is transformed as follows:

$$-\frac{\partial \psi_B}{\partial C_A} > \frac{RT}{C_B C_A^e}. \tag{18}$$

As function ψ_B does not change sharply with a variation in C_A at low values of C_A^e, the inequality (18) is disturbed. Consequently, on increasing the concentration of component B, a rise in the concentration of element A ($\delta C_A > 0$) is possible only in a certain ranges of composition of the impregnating mixture. It should be noted that an increase in the concentration of element A is also possible when $f < 0$ (see [12]).

On the basis of the plot of ζ_0 versus ζ_0 (C_A) given in Fig. 6 and from the analysis given above of the influence of the concentration of B in the active mixture on the boundary concentrations of elements A and B in the bulk of the substrate metal, the nature of the variation of $\xi_{0, A}$ with the concentration of component *B* in the mixture, C_B, can be determined (Fig. 7).

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*It is assumed that $f > 0$.

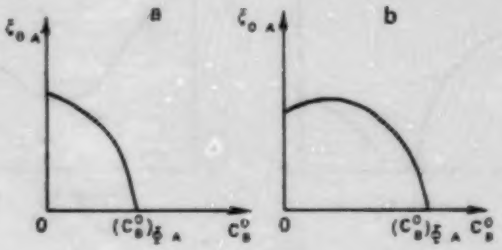

Fig. 7. Variation of $\xi_{0, A}$ with the concentration of component *B* in the mixture.

The concentration $(C_B^0)_{\Phi, A}$ determines the concentration of the component *B* in the mixture, when $C_{s, A} = C_{1, A}$ (Fig. 7, a), i.e. a phase transformation of the base metal does not take place under the influence of element *A*. Another case is shown in Fig. 7, (b), where there is no monotonic reduction in the limiting concentration of the element *A* when the concentration of *B* is increased. A case of monotonic reduction in the limiting concentration of element *A* is shown in Fig. 7, (a). On the basis of the curves given in Fig. 7, the possible types of plots of composition of the mixture versus thickness of the diffusion layer can be divided into two classes. The first type is shown in Fig. 8, (a) and the second in Fig. 8, (b).

We shall now provide some experimental data in support of the mechanism proposed above.

The chemical potential of the diffusion source during one-component diffusion saturation was varied by introducing a passive additive (Al_2O_3) whose concentration in the impregnating mixture varied from 0 to 100%. Diffusion coating was carried out in two variations—in the presence and in the absence of ammonium chloride. Diffusion coating of titanium without an NH_4Cl addition was found impossible, while chromizing in the absence of NH_4Cl did proceed, but at a very slow rate. Introduction of a gas-forming additive significantly intensified diffusion coating by these and other similar elements. This is an excellent example of the effect of a passive additive. The effect is quantitative in nature and does not change either the nature or phase composition of the diffusion layer.

The results obtained are given in Fig. 9. It is obvious that the nature of the curves in Figs. 7 and 9 is identical. The only exception is for aluminizing (Fig. 9, c). In this case on changing the potential of the diffusion source, not only the thickness of the diffusion layer but the phase composition of the layer also changes. When the concentration of aluminum in the mixture is less than 50% an α-phase layer of small thickness is formed. Reducing the

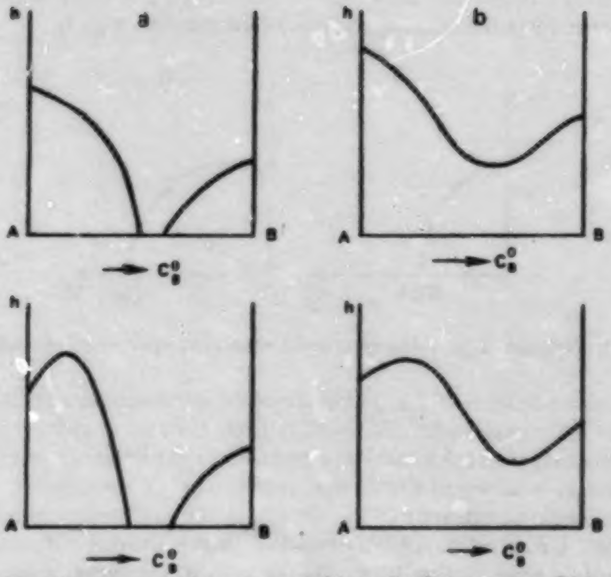

Fig. 8. Possible types of plots of composition of mixture versus thickness of diffusion layer:

a—First type; b—Second type.

quantity of Al_2O_3 and increasing the aluminum content results in the formation of fairly thick diffusion layers consisting mainly of aluminides of iron. In the presence of NH_4Cl, the concentration range for the formation of aluminides further widens. Such a sharp variation in the concentration of aluminum in the diffusion layer cannot but be reflected in its diffusion mobility. The results obtained can be easily explained by taking into consideration the concentration dependence of the diffusion coefficient.

The second point to be explained is the effect of the chemical potential of the diffusion source on the extent of two-component impregnation. The potential of the diffusion source in such a case varied due to change in the composition of the mixture and also due to the introduction of an activator (NH_4Cl). This phenomenon is also observed in systems of types III and IV in which a chemical interaction among the diffusing species in the impregnating mixture is virtually absent. The results obtained have been discussed in sufficient detail in the preceding section. Supplementary experimental data which takes into consideration practically all the principal types of interactions, is given in Fig. 10.

From an analysis of the data given above, it is possible to optimize the conditions for obtaining plots of types I and II.

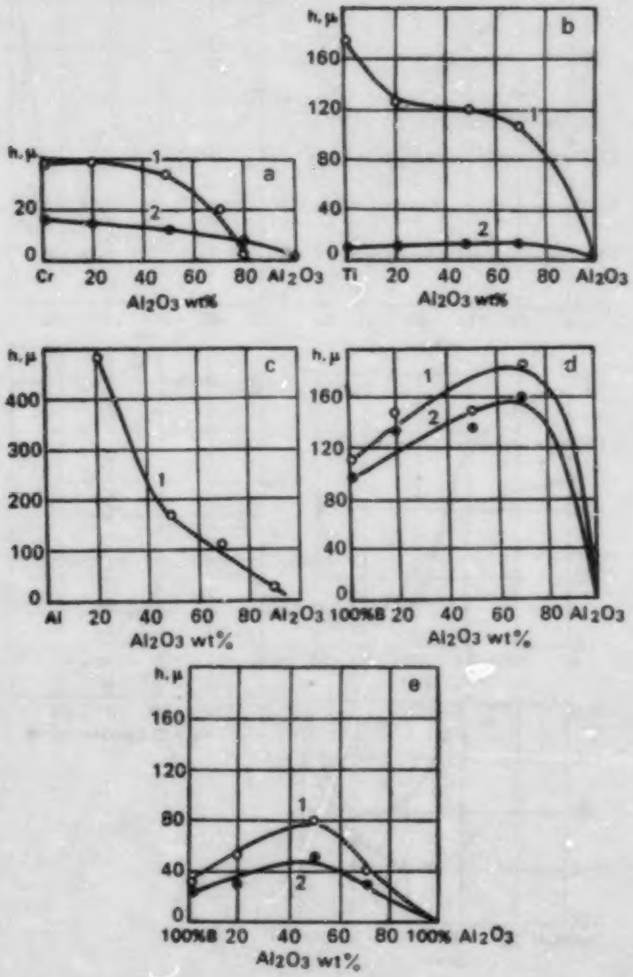

Fig. 9. Effect of a passive additive (oxide of aluminum) on thickness of diffusion layer ($t=1000°C$, $\tau=6$ h):

a, b, d—mixture with activators (2% ammonium chloride); c, e—mixture without activators (1—Armco iron, 2—steel 45).

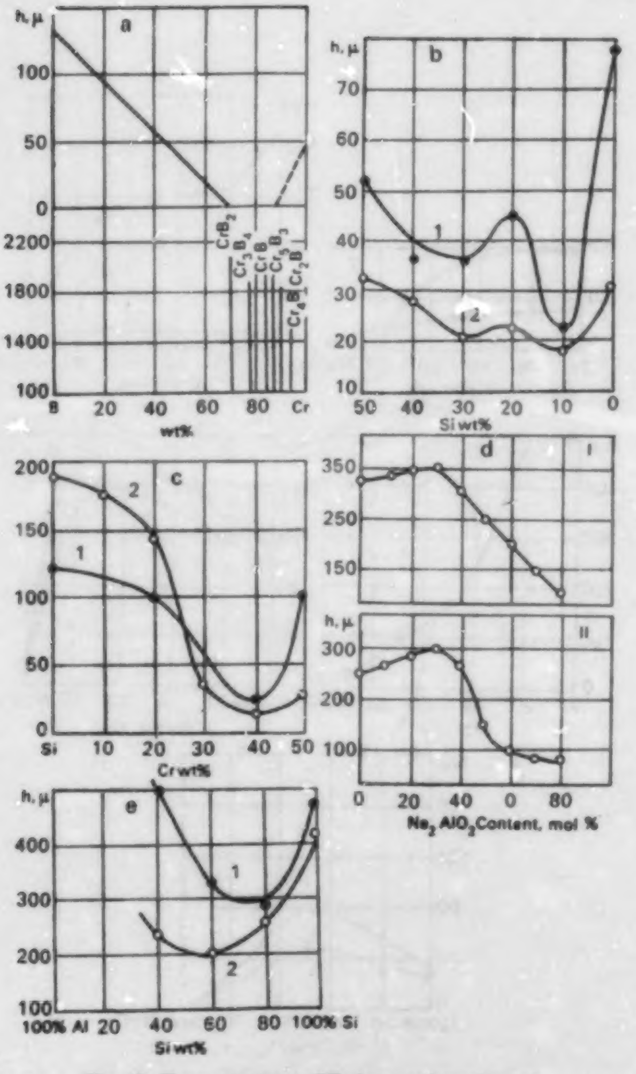

Fig. 10. Two-component diffusion coating of metals:

a) borochromizing of Armco iron in powdered boron and chromium without activator; b and c) borosiliconizing and chromosiliconizing of (1) molybdenum and (2) tungsten in powders of elements with 2% of activator (b: $t=1000°C$, $\tau=3$ h; c: $t=1050°C$, $\tau=5$ h; d: electrolytic boroaluminizing of Armco iron at a current density of 0.35 A/cm^2 (I—1050°C, II—950°C, $\tau=3$ h); e: Aluminosiliconizing of (1) Armco iron and (2) steel 45 in powders of elements with 2% of activator ($t=1000°C$, $\tau=6$ h).

Curves of type I are obtained in the following cases:

1. When both the impregnating elements from chemical compounds of fixed composition with the substrate metal, the compounds being insoluble in the pseudobinary system (systems: W–C–N, Nb–B–C, and others [10–12]).

It should be noted that, in such cases a change in the method of impregnation does not cause any variation in the type of plot of the composition of mixture versus thickness in the diffusion layer.

A very common example of this class is a system in which one of the impregnating elements forms a stable intermetallic compound of fixed composition and the other forms a solid solution* with the substrate metal as a matrix. The phases mentioned are practically impermeable to the second component. For diffusion coating of iron some of the systems with boron as a component can be placed in this category, namely Fe–B–Cr, Fe–B–Mo (W), Fe–B–Cu and others (Fig. 10, a).

2. In systems where every diffusing element has a limited solid solubility in the base metal, the potential of the active medium is, however, such that in a certain range of compositions of the impregnating mixture, the quantity of the elements entering the layer is not sufficient for new phase formation (see Fig. 3, b). This case differs from the first example mainly because a change in the method of impregnation can lead to a variation in the type of the plot of composition of the mixture versus thickness of the diffusion layer. In other cases, plots of type II, as shown in Fig. 8 (b), are obtained. Examples of specific plots of a similar type are given in Fig. 10 (c, e). The position of the minimum on the plot of composition of the mixture versus thickness of the diffusion layer is determined by the diffusion mobility of the impregnating elements. The minimum of the thickness of the diffusion layer moves in the direction of the slower diffusing element with the extent of shift in the position of the minimum [1] being inversely proportional to diffusion mobility. The experimental results of the present work very well illustrate this situation.

The deviations observed in practice, in realizing the type of plots indicated above may be attributed to the concentration dependence of the coefficient of diffusion and also to the effect of coefficients in the cross diffusion terms.

5. SOME CHARACTERISTICS OF THE FORM OF MEDIUMS USED FOR MULTICOMPONENT IMPREGNATION

Impregnation Using Powder Mediums

Powder mediums are the oldest and most-widely studied diffusion sources. It may be pointed out that multicomponent as well as one-component diffusion saturation in active powder mediums is based on two processes taking place in the mixture: 1—dispersion of the active component throughout the bulk of the mixture by means of gases filling the pores (this process plays a very important role in highly active and effective mediums and 2—solid-phase diffusion with more or less close contact between the mixture and the metal substrate.

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*This refers to solid solution formed as a result of phase crystallization during impregnation.

Many investigators are of the view that the role played by solid-phase diffusion of an impregnating element from a powder into a metal is negligible and needs little or no consideration. It is thought that the active element, being a part of the powder mixture, on heating, reacts with gases present in the pores of the charge and the compound so formed fills these pores, in particular those which are close to the base metal. The catalytic action of the surface of the metal favors the formation of active atoms of the diffusing species. Reference [45] provides an example. These authors studied the process of "solid-phase" boronizing of steel by one of the widely available boron-bearing materials—boron carbide. Commercial grades of carbide contained boric anhydride—B_2O_3 as an impurity. It has been established [45] that boriding does not take place in boron carbide powder from which boric anhydride has been washed off. A study of the composition of the furnace atmosphere during diffusion coating in a B_4C medium enabled the authors to conclude that the interaction between carbide and boric anhydride leads to the formation of a carrier gas (monoxide of boron, B_2O_2) in the absence of which the process of diffusion saturation practically stops.

The authors of [46] consider that during impregnation of graphite with molybdenum or tungsten from oxides of these metals, a decisive role is played by the high evaporability of the oxides which ensures the transport of metals to the surface of graphite. Similarly, it is considered that gas-phase impregnation is an integral step in the so-called 'powder' processes.

However, the views quoted here should not be accepted as absolutely reliable. For example, from this it follows that the intensity of formation of an active gas carrier in the pores is determined, to a large extent, by the gas-powder interface, i.e. by the size of the powder particles. Moreover, for every powder mixture there is a limiting temperature above which the degree of dispersion of the mixture does not influence the extent of impregnation [46]. At this temperature, the surface diffusion is so active at the points of contact between the powder particles and the metal that the role of the gaseous carrier is reduced to a minimum. The authors of [47] have mathematically shown that, irrespective of the nature of the surface, surface diffusion proceeds very rapidly and the only factor which can prevent it from playing a decisive role is the restricted area of the surface itself. At the same time, these authors assert that according to the theory of probability, by increasing the contact area between the reactants the rate of solid-phase reaction cannot be increased more than three times.

In [48], a plausible mechanism of the reaction between an active powder and the surface of a metal is suggested: "when sufficiently small particles come in contact with each other, a bond is created between them due to a negative pressure at the point of contact and a liquid like coalescence, i.e. a faster bonding with material transport to the joint commensurate with the mass of the particle itself. This effect plays a significant role during sintering of a metal powder system as a result of a chemical reaction, i.e. when the particles are very small". It is understandable that the effect should be significant (pronounced) if the compacted metal plays the role of one of the surfaces during the reaction. In the case of multicomponent diffusion coating the special feature of the mechanism described should be that active microparticles of more than one 'kind' simultaneously appear on the surface of the metal. If their ratio does not quantitatively influence the nature of the layer, for example, during impregnation with two α-stabilizing elements, resulting in a layer of stable ferrite irrespective of the composition of the mixture, the mechanism of the process of its formation remains the same as in the case of a one-element process. The distinction appears only when there is a possibility of formation of a ternary compound in the corresponding ternary system at a stage closer to equilibrium. The stipulation regarding the 'encounter' of two or more kinds of microparticles, practically at one point, on the surface of the metal, renders the likelihood of formation of such a compound less probable and binary compound is formed by that diffusing species which has either a higher concentration or a higher chemical affinity toward the substrate metal. The second diffusing species may, if such a possibility exists, only form a solid solution in this compound.

Carburizing is considered to have been exhaustively studied and it is generally accepted that during carburizing, in a solid-phase carburizer, carbon monoxide plays the role of the main carrier of carbon. Although the process is apparently well understood, the authors of [49] subjected it to tests by carrying out carburizing with wood charcoal in an atmosphere of argon. The following were observed:

1. In the absence of an intimate contact between the carburizer and the metal, carburizing does not take place;
2. When there is such a contact, the process obeys the same kinetic laws as are applicable to 'solid' carburizing, but at a slower rate.
3. The process is sharply intensified, if highly dispersed carburizer (acetylene black) is used and densely packed by ramming around the workpiece and if the metal has undergone plastic deformation.

Thus, at fairly low temperatures, as compared to normal carburizing (below 1000°C), the process of solid-phase surface diffusion can play an important and, sometimes, even decisive role during carburizing. The same can be said of other powder processes such as metallothermic reduction.

Extensive studies on multicomponent diffusion coating by aluminothermic reduction of mixtures of oxides of elements to be impregnated have been carried out in the department of Physical Metallurgy at the Baikov Polytechnic Institute.

Results of some of the studies on impregnation by an aluminothermic process, especially related to combinations of elements which have not been extensively studied will be given in the chapters dealing with the specific processes of impregnation.

One of the serious shortcomings of the powder method in its industrial application could be that the surface of the work piece cannot be covered with the powder. One of the variations in powder methods known as the dross method [50], is free from this drawback. In this method, a suspension containing powders of impregnating elements in the form of small particles is applied on the surface of the work piece. This is followed by drying and diffusion annealing. In principle, this technique does not differ from normal powder impregnation.

In the literature on multicomponent diffusion coating in a powder medium, special attention is paid to the effect of the composition of the mixture on the depth, structure and properties of the resultant diffusion layers. There is very little data on modes of impregnations. A comparison based on the data of [50–52] could be of great interest here. In these investigations, in addition to other data, results of studies on the effect of modes of impregnation on thickness of the diffusion layer have also been given. For example, in [50] data of the effect of the temperature of impregnation on aluminosiliconizing of a nickel alloy has been reproduced. From this, it follows that there must be a temperature at which the thickness of the diffusion layer remains unchanged irrespective of variations in the composition of the mixture from pure silicon to pure aluminum. According to our analysis of their graphs, this should happen at 1000°C. In [29] and [53], results of three-component diffusion saturation with a fixed concentration of one component and variable concentrations of the other two diffusing species have been given. In both these cases there are compositions of mixture at which any variation in the ratio of two diffusing species does not alter the thickness of the layer. Thus, in [50] this has been explained to have been observed by varying the temperature of impregnation and in the other two cases by the introduction of a third impregnating element. Except for boron, all the diffusing species were α-stabilizing elements. During surface impregnation with these elements by the term 'thickness of diffusion layer' is meant the distance from the surface up to the concentration discontinuity indicating the boundary of the stable ferrite layer. During complex diffusion saturation of the layer, with the characteristics of a multicomponent (3 to 4 components) α-solid solution, it is possible to establish such a ratio of concentration of the components when the net effect of surrounding the γ-region by them remains unchanged. Apparently, it can be assumed that under these conditions accelerating or retarding effects of individual diffusing species on the rate of diffusion compensate each other. From this statement, it follows that this type of effect of variation in temperature and concentration of the solid solution on the diffusion mobility should be same; in either case, both the degree of imperfection in the structure (vacancy-dislocation system) and the spatial energy distribution of electrons of the metal, i.e. the type of interatomic bond are affected.

Lastly, it is necessary to analyze the data on feasibility of the use of stable compounds as diffusion sources.

The high-temperature (900–1500°C) interactions of zirconium beryllide $ZrBe_{13}$ with tungsten and molybdenum have been investigated [39]. It was found that these compounds which are similar and refractory (melting point approximately 1650°C) can serve as very active diffusion sources of beryllium (it does not serve as a source of zirconium, apparently, on two counts: beryllium has a much higher diffusion mobility and its concentration in the source is also very high); on interaction beryllides of the base metal are formed. No data is available on the extent of their alloying with zirconium. However, it is certain that a stable compound, in solid state, can serve as a highly active diffusion source without the aid of any activators. Many investigators consider monocarbides of groups IV and V transition elements as most stable among all the known materials. However, the authors of [40] have established that, on the addition of tantalum monocarbide to 'Pobedits' (a proprietary cermet used in the USSR) of the VB type, the former decomposes, not due to dissolution of tantalum in the alloy–tungsten carbide (WC) base, but due to the formation of a bonding with cobalt. Thus, a superstable monocarbide of tantalum, TaC, at a temperature several hundred degrees lower than its temperature of decomposition can be a diffusion source of tantalum.

Very interesting data has been given in [41] and [42]. These authors have investigated the interaction of a very stable compound—boride of titanium, TiB_2 with transition metals: zirconium, vanadium and titanium itself. It was established that a highly stable boride serves as an active diffusion source of boron: on interaction in a vacuum a layer of boride is formed on the surface of the metal. The extent of impregnation depends on the degree of dispersion of the reagents and reaches a maximum value in their pulverized state. It has been demonstrated that boriding with titanium boride takes place not only on zirconium or vanadium (the latter is more significant since boride of titanium is much stronger than the compound of vanadium with boron) but on titanium itself: in this case the high concentration gradient of boron across the titanium boride–titanium interface serves as a driving force for the diffusion process.

Siliconizing of carborundum and boriding by carbide of boron in contact with steels are well known and no reference to literature is necessary. The aforementioned carbides can serve as diffusion sources under conditions of intimate contact with the base metal. In [43], it has been stated that at sufficiently high temperatures (for contact with steel, 1400°C) carborundum can be a source of not only silicon, but even of carbon. The processes taking place close to the surface of the steel in such a case, are very complex. The overall result is the emergence of a 'secondary' film of silicon carbide, with a good bonding with the metal. Based on this, it has been well established that silicon and carbon enter the metal individually and later interact on its surface and the layer obtained is practically without defects and impermeable with respect to diffusion. Excess silicon separating out from carborundum does not diffuse through the layer and no silicides are formed under it.

In [44] it has been pointed out that stable compounds of one more kind, i.e. borides of rare-earth metals of the lanthanide group, can serve as a diffusion source of boron and boron only because it is abundant (in quantity).

Diffusion Coating in Gaseous Mediums

Thermochemical treatment in a vacuum is one of the variations of diffusion saturation in gaseous mediums. It is necessary to take into consideration the following important conditions: thermochemical treatment in a vacuum and diffusion saturation in a so-called vacuum are completely different from each other. For diffusion coating the pressure inside the furnace is reduced with the aim of replacing the air by an active gas at a much lower pressure, i.e. the atmosphere of the furnace is not removed but substituted with the object of facilitating the addition of diffusing species in the metal, in the most suitable form for adsorption.

Thermochemical treatment in a vacuum, at first sight may only appear to be the most 'pure' and simplest form of impregnation. Being simultaneously subjected to the interaction of high temperature and low pressure, many active mediums exhibit characteristics which are absent under normal conditions, for example, during diffusion saturation in pulverized mixtures with gas-forming additives. As an example of easily volatilizable diffusing species during impregnation under low-pressure conditions, the authors of [54] investigated the interaction of amorphous boron with nine refractory transition metals in a vacuum—molybdenum, tungsten, titanium, zirconium and others. It was found that on replacing argon gas, at a pressure close to that of atmospheric pressure, by a vacuum, the rate of growth of the diffusion layer of borides increased by 5–10 times, subject to the condition that only high-purity boron was used.

Thus, the advantages of the vacuum process (it will be better to call it diffusion coating at reduced pressures, as the atmosphere in the furnace is not completely eliminated) become apparent only on fulfilling certain special conditions, the most important among them being the high purity of the diffusing species (free from impurities which hamper its transport in a gaseous state). This also refers to the surface of the metal which should also have a high degree of cleanliness. If this condition is not fulfilled, vacuum diffusion coating would still be possible but will proceed at a very low rate. The work described in [55] can be given as an example of multicomponent diffusion saturation in a vacuum (at residual pressures in the furnace in the range of 10^{-2}–10^{-3} mm Hg). For simultaneous diffusion coating of a number of alloys by chromium and aluminum, it appeared necessary to prepare a chromium–aluminum master alloy with a predominant concentration of chromium (80%). During attempts to use a mixture of aluminum and chromium powder, only aluminum impregnation took place owing to the fact that its partial pressure on sublimation is considerably higher than to that of refractory chromium. This is apparently applicable in all cases of multicomponent diffusion coating at reduced pressures, with evaporation of components and their delivery at the surface of the metal by the vapor phase. In other words, although this method has some advantages, it does suffer from certain drawbacks. Among these, the first is that the diffusing species should easily volatilize in a vacuum (for vacuum chromoaluminizing the authors of [55] had to use temperatures of 1150 to 1400°C and soaking times of up to 18 h) and the second is that their chemical affinity for the base metal should not differ greatly so that there is a distinct possibility of a two-component, and not a one-component, diffusion saturation. It is necessary to point out that for demonstrating the versatility of the vacuum method the authors of [55] simplified the technology of the process by substituting the pulverized source by pieces of master alloy, placed at a considerable distance from the workpiece.

The largest number of investigations have been devoted to the production of two- and multicomponent diffusion layers in mixtures of gases, every one of which is the source of one diffusing species. The possibility of formation of chemical compounds in the active mixture which may prevent subsequent diffusion in the base metal is less likely in such a case as compared to liquid or pulverized impregnation methods. It is clear that gas-phase impregnation implies a reaction between the gas and surface of the metal as an inherent step, owing to which the formation of compounds is possible only in the growing layer. Thus, the nature of the diffusing species does not lay any special restrictions on the gas-phase process of multicomponent impregnation. The basic problem is that in every case it is necessary to study the complete concentration range in order to obtain a layer of optimum structure. The properties of gases are considerably variable as compared to those of solid materials and all the technological factors very significantly affect the results of the process.

A convincing example of exploiting the advantages of the gas-phase method of multicomponent impregnation is given in [56]. A mixture of chlorides of titanium and tungsten has been used as a source for impregnation by tungsten and titanium, which would have been almost impossible by any other method. It has been shown that diffusion saturation of such metals, which exhibit a very low diffusion mobility, can be accomplished with the help of the gas-phase process. However, to achieve this, it would be necessary to select the conditions of impregnation in such a way that equality in the rates of condensation and diffusion is maintained.

Multicomponent diffusion coating by the gas-phase method can be successfully carried out using one of the active gases as a carrier of not only one but two diffusing species to the metal surface. For example, Govorov [57] carried out carbonitriding over a wide range of temperatures (from 500° to 900°C) by passing ammonia through a layer of solid carbon (wood charcoal). A mixture of the products of reaction of ammonia and coal along with the unreacted ammonia was fed to the surface of the metal. It resulted in an increase in the reaction rate by 2 to 3 times.

The extent of the influence of the composition and structure of the base metal on the results of one-component diffusion coating by ths gas-phase method has been demonstrated [58]. Treatment of metallic chromium, obtained by a powder-metallurgy method, with a mixture of propane and hydrogen results in the formation of a chromium-carbide layer. However, if the metal is taken in the form of a thin film, obtained by vacuum deposition on cold glass, under identical conditions of impregnation transparent chromium hydride is formed. Hydrogen interacts with the metal, though not as actively as carbon (it is known that the carbides of transition metals are much stronger than their hydrides) but the diffusion mobility of a small ion of hydrogen is certainly much higher than that of carbon. Only complete replacement of the gaseous mixture by propane enables us to obtain a carbide layer in place of hydride. It has been shown, in this case, that only one carbide is formed (Cr_7C_3—most stable) and its electrical conductivity is higher, by one order, than that reported in handbooks corresponding to the compound obtained by powder-metallurgy processes. Thus, by a proper selection of impregnation conditions, the gas-phase surface alloying method makes it possible to obtain a diffusion layer—much closer to a state of equilibrium than any other methods.

Unfortunately, among the very few studies devoted to multicomponent gas-phase impregnation, there has been practically no investigation of the effect of composition of the gaseous mixture over the whole concentration range (from one pure gas providing one-element impregnation to the other). Some authors have studied the impregnation of tungsten by nitrogen and carbon in a mixture of ammonia and benzene vapors. It was found that due to a mutual insolubility of carbides and nitrides of tungsten (especially due to the insolubility of nitrogen in carbides of tungsten), nitriding takes place in an ammonia atmosphere, while in an atmosphere of a mixture of ammonia and benzene only a carbide layer is formed. In pure benzene (diluted with hydrogen) only a layer of carbides is formed, but with a considerably larger thickness and a higher content of higher carbide, WC. Thus, in the latter experiments, ammonia played the role of only a diluent of active gas considerably reducing the potential of the diffusion source.

In many cases gas-phase impregnation of steels is considered one-component impregnation when the gaseous medium, consisting of a gas 'diluted' with a considerable amount of hydrogen, is the diffusion source. Hydrogen is not considered to be a source for diffusion saturation. Moreover, its high solubility in iron and its adverse effect on the properties of iron are also well known. This effect can perhaps be neglected when a metallic layer, exhibiting no solubility for hydrogen, is formed at a fast rate on the metal surface. In this respect, the investigation [59] is interesting. Here, the authors replaced the normal gas metallizing medium consisting of a mixture of hydrogen and vapors of the volatilizable chlorides of transition metals, by a mixture of vapors of these chlorides produced directly in the furnace as a result of reaction between the metals (titanium and chromium) with carbon tetrachloride (CCl_4). The absence of hydrogen, hydrogen chloride and ammonia in the furnace atmosphere has a very positive effect on the properties of the resultant layers consisting of carbides of titanium and chromium in solid solution.

A number of investigations by Arkharov are of considerable interest from the point of view of understanding the principles of gas-phase multicomponent diffusion saturation of metals. For example, in the investigations [60, 61], most probably for the first time, the possibility of the use of atmosphere air as a source for two-component impregnation was indicated. During this investigation, on the surface of chromium a layer consisting of two zones was formed—the nitride, Cr_2N, adheres to the surface of the metal and above that forms the oxide, Cr_2O_3, with a higher lattice constant than the normal (due to dissolution of nitrogen). In [62, 63], simultaneous diffusion saturation of carbon and nitrogen in chromium has been studied where commercial molecular nitrogen was used as the source of diffusion species. The nitrided layer in this case was situated at the diffusion layer-metal interface and the carbide layer (Cr_3C_2 on the top and Cr_7C_3 below that) at the surface.

On the basis of these analyses, in spite of the limited amount of experimental data being available, it is possible to draw some conclusions on the potential of the gaseous method of multicomponent impregnation.

However, the principal advantage of the gas-phase method, namely, the high rate of impregnation, is almost completely negated by its well-known drawback, namely, the necessity for complex and hermetically sealed equipment. (This is further complicated especially when the active gases are not stable and are corrosive and they should not only be isolated from the air but also are required to be produced for their immediate utilization.)

Impregnation in Liquid Mediums

An active liquid medium, especially a molten bath, is characterized by the fast rate of interaction taking place in it. Liquids are practically equivalent to solid pulverized materials as regards density while, at the same time, the intensity of mixing of their constituents and rates of various chemical reactions taking place in them, they differ little from gaseous mediums. Bearing in mind that in multicomponent impregnation, the process of intensive mixing of the components of a complex medium is of great importance due to the necessity of maintaining the supply of all the constituents to the surface of the metal, we may appreciate the importance of liquid impregnating mediums for effective multicomponent impregnation.

Two types of liquid impregnation mediums may be used. One of them is a medium based on molten metals. For thermochemical treatment, attempts were made to study baths where the molten metal served only as a solvent for the element to be used for surface alloying [64, 65]. This method has all the advantages of a molten metal both but suffers from a serious drawback which renders its use in industrial application difficult. For active diffusion of the diffusing species, dissolved in the bath, in the base metal, a high temperature is normally required. It is however, difficult to find a metal which will dissolve large quantities of the diffusing species and, at the same time, not interact with the metal substrate. In multicomponent impregnation the problem is further complicated, i.e. it is necessary to find a solvent suitable for a number of simultaneously diffusing species.

The second method of surface impregnation using a molten bath is based on the use of a metal which serves as the basic constituent of the bath and is also the main diffusing species.

The authors of [66] have established that, during condensation of aluminum vapor on metals, heated below 658°C, it may not be completely absorbed. However, a slight superheating above the melting point not only ensures absorption but also results in a very intensive growth of the diffusion layer. The authors of [67] have pointed out that the advantage of using a molten bath of diffusing species is not easy to exploit in multicomponent surface alloying: it is very difficult to find a system of diffusing species, where all the components are low melting and do not adhere to the metal (i.e. where an optimal moderate wetting of the metal can be ensured throughout the concentration range). Further, they should exhibit mutual solubility in the liquid state and should adhere on diffusion saturation, should result in a surface layer with an optimum structure and properties. One such method namely galvanizing of steel in a zinc melt [68] has found wide practical application. In this work there is no data on multicomponent impregnation in molten baths. West German investigators [69] have studied the effect of various additions to a galvanizing bath on the corrosion resistance of the obtained coating. Additions of tin, lead, aluminum, titanium and copper were made to the melt. It was found that surface alloying of steel simultaneously with zinc and small amounts of copper and titanium provided a coating with the best possible resistance to aqueous and atmospheric corrosion. The authors of [69] ascertained that introduction of aluminum in the galvanized layer has little effect on its durability; on the other hand, in [70], it has been pointed out that introduction of 2 to 5% of aluminum in the melt improves the corrosion resistance of galvanized steel. Thus there does not seem to be any clarity on 'multielement galvanizing'. The authors of [71] have, apparently made a detailed study of the effect of aluminum on galvanizing by using metallographic methods. They have shown that aluminum, being an α-stabilizing element, hinders the formation of zincides and assists the formation of a thick layer of solid solution of iron in zinc and a thick layer of zinc adhering to steel over layers of zincides. Although this effect is generally destructive, it, however, can be transformed into an advantage by diffusion annealing. Adherent zinc is resorbed and transforms to an 'acicular' zincide layer (texurized like a boride layer) and exhibiting high corrosion resistance.

The method of diffusion coating of steel with aluminum, in a molten bath of its alloys, has also found some application. On the basis of our own experience of investigations on this bath, we can point out that its main advantage is a very high content of the diffusing species in an active state, easily becomes its principal drawback. There is practically no method of preventing dissolution of steels in aluminum or at least to prevent adherence of aluminum to steel.

There are a large number of processes, associated with diffusion at high temperatures, which are not possible without a liquid phase. For example, Mirkin [72] succeeded for the first time in obtaining a surface-impregnated layer with a high concentration of tungsten on steels by irradiating tungsten powder applied on steel by pulsed laser rays, thus achieving what was earlier considered impossible, viz. the melting of tungsten and its active diffusion in steel.

Gudremon in the monograph *Spetsial'nye stale* (Special steels) [73] confirms that the presence of low-melting inclusions and metals less soluble in iron (for example, lead), in the structure of steel, when sufficiently well dispersed, must significantly facilitate diffusion processes in the metal, either as a result of diffusion transport in the bulk of a liquid-metal drop (at a temperature higher than the melting point of the inclusion) or due to diffusion along the drop-matrix interface. The very high rate of diffusion of drops of lead in heated steel supports this view.

Thus, from the above description of molten baths, it can be seen that they are the most effective diffusion sources [74, 75]. However, fused salts are more suitable for multicomponent diffusion coating. The fact that the potential diffusing species is generally in the form of a compound (and that too in a very strongly bonded form), can be considered a drawback. (We are not talking of those out-dated baths where the potential diffusing species were contained in the solid form in a suspended state.) However, this very 'drawback' becomes an advantage, since this enables us to vary the results of impregnation over a very wide range, by influencing the behavior of the bath by different methods.

In this respect, salt bath and, in particular, glassy mixtures of fused oxides, are most suitable for investigation, control and application.

Potential diffusing species, contained as oxides in salt baths, can be reduced by applying an electric field or by a chemical reducing agent (with a higher chemical affinity for oxygen as compared to the diffusing element).

The fundamentals of the theory of electrolysis of fused salts during thermochemical treatment, considering salts as ionic solutions, have been described by us in [76] and their applications in simultaneous reduction of more than one oxide in complex melts are given by Sherbakov in [77].

In [78] the authors have studied multicomponent surface alloying by an electrolytic technique. Practically all the processes of multicomponent thermochemical treatment, starting from the process of electrolytic boriding, have been investigated. A fused bath of sodium tetraborate (borax) has good technological properties: it has sufficiently low melting point, is reduced in an electric field of low current density and exhibits high dispersion, protects the workpiece from corrosion (pitting) due to potential difference it is not positioned correctly with respect to the anode. As a rule, surface impregnation of steels with boron was studied in combination with metals and nonmetals, which form such solid oxides at the temperature of impregnation, and exhibit a high solubility in a borax melt.

Equilibrium diagrams for borosiliconizing, borochromizing, boroaluminizing, chromosiliconizing, aluminosiliconizing and other similar processes have, qualitatively, a similar appearance (Fig. 11). Presently such plots are only available for a very few pairs of elements over a very limited range of temperature, whereas it is known that the temperature of the process can

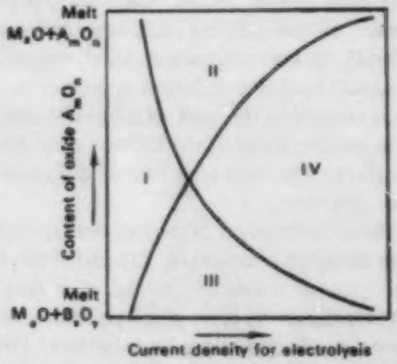

Fig. 11. Qualitative nature of equilibrium diagrams of two-component diffusion saturation during electrolysis of melts of oxide systems M_aO–A_mO_n–B_xO_y (where M_a—alkali metal, and A and B are diffusing species):

Zone I—Diffusion layer absent; Zone II—Impregnation of cathode metal by the element A; Zone III—Impregnation by element B; Zone IV—Simultaneous impregnation by diffusing species A and B.

influence the results of electrolysis (does not have as much effect on the thickness of the layer as on the ratio of components in it) as much as the composition of the active medium [79]. It may appear that the authors of this work have established something quite obvious. Nevertheless, it had practically remained uninvestigated quantitatively. On decreasing the temperature of reduction of the complex electrolyte, the content of the more electronegative of the component, i.e. of the more easily reducible diffusing species, increases in the formed layer. This is understandable because the electrochemical reaction taking place is a peculiar case of a 'simple chemical' process where the kinetics depend significantly on the temperature.

The general correlation between temperature, kinetics and the structural constitution of diffusion layers in electrolytic to processes, have not been well studied. The data given in [78] is, therefore, of considerable interest. The authors have ascertained that at a certain composition of the bath for electrolytic chromo-siliciding, any increase in the process temperature above 1050°C results, not in an increase but, on the contrary, in a decrease in thickness of the layer of solid solution of chromium and silicon in ferrite. This cannot be attributed to any factor other than the variation in the ratio of the diffusing species in the layer and corresponding changes in their effective diffusion mobility: apparently, the rise in temperature improves the conditions of reduction of the more electropositive chromium, which has a lower mobility in solid solution than silicon, and hence lessens the extent of encircling of γ-region of iron.

A considerable amount of work on simultaneous electrolytic impregnation of steels with boron and other elements has been carried out by Pasechnik et al. [80–83]. Summing up the results of these investigations, it is observed that they have illustrated the possibility of simultaneous reduction of boron and other elements, such as chromium, aluminum and zirconium which are known to form refractory oxides, from borax-based melts. The layer consists of borides of iron and other such phases formed during the interaction of the second diffusing species with iron or carbon dissolved in the steel (carbides of chromium during borochromizing of carbon steels, α-phase during borosiliconizing, boroaluminizing and borochromizing of low-carbon metals). Certain doubts have arisen based on x-ray structure analysis according to which, in a number of cases, the products of interaction between boron and the other diffusing species (active boride-forming) have been found in the diffusion layer (for example—borides of chromium and zirconium).

Processes of multicomponent diffusion coating using an electrolytic technique, especially in liquid electrolytes, certainly merit further investigation, since they provide certain advantages unattainable by any other process: it is possible to achieve such energy inputs in the reaction mixture, which may be required to dissociate any potential diffusing species, to the free state, from whatever stable bonding it may have developed.

For investigations as well as for applications the silicate type salts, containing one ionic glass former and a few cations of alkali metals, are the simplest. However, even in such a simple case the space-energy distribution of bonding electrons is complicated. For example, the oxygen ion varies its effective charge, on substitution of one alkali by another and depending on the structural form in which it exists, its location and, further on the variation in the quantity and nature of glass-forming ions [84]. On the whole, it can be assumed that in multicomponent glass the net binding energy of oxygen and glass formers is quite low (in fact, this is the principle of the cryoscopic effect). However, no quantitative evaluation of this phenomenon is available [85]. In fact, each complex silicate-type system will require a separate investigation.

In [86], it has been established that at moderate concentrations of alkali oxides in glasses of the B_2O_3–P_2O_5 system (these were used by us for borophosphiding of steels) there is a homogeneous distribution of glass-forming ions [B^{3+}] and (P^{5+}) in the substructure, i.e. in the structure the constituents are components of types (PO_4) and (PBO_4) and not (BO_3) and (BO_4). At the same time, two 'microphases' can be observed in borosilicate glasses as follows: a highly refractory siliceous skeleton, which increasing the viscosity of glass, with intermediate spaces filled with oxides of sodium and boron–oxygen complexes. However, according to the authors of [87] this corresponds to a temperature in close proximity to that of the zone of melting of glass (approximately 700°C) and the size of microphase spaces ranges between tens to hundreds of angstroms. Apparently these should decrease on increasing the temperature, while the mobility of its constituent should increase and, therefore, the extent of mixing of oxides of boron and silicon may be considered fairly high for the temperature range for borosiliconizing. In [88], it has been established that, in glass production, a widely used compound of the system as oxides of germanium should be very compatible with oxides of silicon. In some cases germanium exhibits a sixfold coordination for oxygen (GeO_6), but in most of cases it maintains a fourfold coordination and the structures of fused germanates are similar to those of silicates. However, we have not observed any case of surface impregnation of steels with germanium, either individually or in combination with some other elements.

The data given in [89] is of great interest in multicomponent impregnation with aluminum and silicon, where it has been confirmed that in lithium–aluminum silicate glasses aluminum and silicon are interchangeable without disturbing the fourfold coordination of silicon and, consequently, without considerable variation in the type and stability of the bonding between the glass-forming ion and oxygen and its reducibility to equimolar ration, i.e. till the replacement of half the silicon by aluminum. Apparently, substitution of lithium glass by cheaper sodium glass should not make any significant difference: the permissible quantity of aluminum may be reduced but, even otherwise, it is generally much less than half.

The compatibility and interchangeability of different oxides in silicate like structures has been exhaustively studied by Krupkin et al. [90]. It was established that oxides of metals and metalloids such as calcium, zinc, barium, lead, tin, etc., cannot be introduced. Al_2O_3 and especially germanium dioxide may be successfully introduced in silicate and borate glasses.

From this it follows that the liquid method of complex impregnation can be successfully applied to many combinations of elements if, at least, one of them is a good glass former. This is especially significant in the case of impregnation with various other valuable elements along with silicon, aluminum and boron. However, many oxides, on being introduced into the melt, increase its refractoriness and therefore, cannot be used in large quantities (for example, oxides of aluminum and chromium). Nevertheless, in this case, a variation of liquid impregnation such as impregnation using pastes can be employed (for example, with high-frequency electric heating). The high temperature of heating and small bath volume enable us to ensure an intensive diffusion saturation even when the glass is, in general, in the form of a paste and not in a molten state [91].

In principle, the liquid bath for impregnation should invariably contain some quantities of solid (fairly refractory) phase, i.e. a deoxidizer. The effect of this material on the structure and behavior of the bath is generally not taken into consideration: to be precise, only its chemical role is taken into account. Moreover, all the physical properties of the melt, which control the fluidity of the bath and consequently, its productivity, are mainly determined by the degree of dispersion and characteristics of these particles, even if the effect of their concentration is not considered. This aspect has been examined by Arkhirov and colleagues [92]. It has been established that, on moderate superheating, a temperature dependence of the viscosity of free-flowing melts is practically nonexistent and their viscosity is almost independent of temperature, whereas on dispersion of solid particles in the bath, a fall in temperature leads to a sharp increases in viscosity. The reason for this is not the particles themselves, whose total volume is very small, but the wetting of their surfaces by the melt. This plays an important role even in metallic melts where suspended oxide particles are feebly wetted by the liquid (there is certainly some wetting, otherwise the oxide particles would have floated upwards). This effect is all the more important in salt baths where a refractory powdered deoxidiser is introduced so that it may interact with the melt. The interaction is preceded by a no less active wetting in which a considerable (as compared to the size of the particles) volume of the melt around it is involved in an atomic interaction with the solid material, i.e. absorbed, and this is fully reflected in the viscosity of the melt. The authors of [92] have indicated that this phenomenon depends on the nature and degree of dispersion of solid particles, i.e. on the total interfacial area and characteristics of the liquid.

Oxides of transition elements are more similar to vitreous oxides than any other class of materials with regard to the type of interatomic bonding. Their insolubility in borates, silicates and other similar melts is well known. This is one of the reasons for rapid impregnation in these mediums [93].

From the foregoing discussion the following conclusions may be drawn. Hitherto, during the investigation of multicomponent impregnation processes, researchers paid the maximum attention, and this continues to be so, to the results of the process; the simple techniques are usually adopted in the laboratory experiments (often pure diffusing agents in powder form are employed): These include application of a multicomponent layer, with the technological feasibility being only of a secondary consideration. As a result, most techniques of impregnation, even though they provide layers of good properties, have not gone beyond the experimental stage. The method of liquid impregnation requires exhaustive investigation, in the laboratory stage, in respect of the behavior of these active mediums and determination of their optimal compositions since their industrial applications present no particular difficulty.

CHAPTER II

Thermodynamics of Multicomponent Diffusion Saturation Processes

The thermodynamics of processes occurring during thermodynamical treatment using either powder mixtures of impregnating elements or their alloys, along with gas-forming activators and also those based on the use of different gaseous mediums has been exhaustively studied and reported on in [94–101, and others].

We are interested in examining the thermodynamics of comparatively recently developed processes for obtaining multicomponent diffusion coatings in mixtures of powder oxides of impregnating elements with metallic or alloy deoxidizers [102–109] and in baths of salts and oxides by the addition of reducing agents or by means of electrolysis [77–78, etc.] is of great practical interest.

1. IMPREGNATION IN POWDER OXIDE MIXTURES USING A METALLOTHERMIC METHOD FOR THEIR REDUCTION

Metallothermic reduction of metals from their oxides is nowadays widely used in metallurgy for the production of titanium, chromium, manganese, vandium, zirconium and other metals and ferroalloys.

Soviet scientists, A.A. Baikov [110], Elyutin [111], Zhemchuzhnii [112], Bogolyubov [113–115], Myrach [116, 117], Klyuchnikov [118] and Pliner [119, 120 and others] have played an important role in development of the basic principles of the processes of metallothermic reduction of metal oxides.

The feasibility of obtaining diffusion coatings on metals and alloys with the reduction of oxides of various metals by aluminum has been indicated in [102–109]. The processes of boriding, chromizing, siliciding, chromoaluminizing, aluminosiliciding and others by an aluminothermic technique have been developed. The use of oxides as sources of impregnating elements has significantly reduced the cost of thermochemical treatment and has also simplified the technology of preparing mixtures for diffusion saturation. However, in our opinion, there is scope for further improvement in thermochemical treatment based on metallothermic reduction of oxides. One such possibility is the use of various metallothermic deoxidizers—silicon, ferrosilicon, ferromanganese, etc. as reducing agents.

The elements of interest in thermochemical treatment, either as reducing agents or reducible oxides, can be arranged in the following order according to the stability of their oxides (beginning with the more stable): Ca, Mg, Zr, Al, Ti, Si, B, Cr, Nb, Mn, V, W, Mo [119]. Every preceding element in this series can act as reducing agent for the oxides of all the subsequent elements. The energy-exchange rate of reducing process is ensured when the difference in the values of potentials required for the formation of oxides of the reducing agent and the element being reduced is of the order of several tens of kilocalories [119].

Reducing agents such as aluminum and silicon, ferrosilicon, ferromanganese and alloys of calcium with aluminum or silicon which are more stable at normal temperatures and are considerably cheaper as compared to pure silicon, calcium and aluminum, are of great interest in thermochemical treatments where their oxides act as sources of impregnating elements. It is well known in metallurgy that the use of complex deoxidizers (calcium silicide, zirconium silicide, silicomanganese) results in a greater cleanliness of the metal than the separate use of individual components of the alloys. Therefore, it can be expected that the use of these alloys will ensure a rapid reduction of the oxides of impregnating elements during thermochemical treatment.

There are two possible ways of using metallothermic reactions during thermochemical treatment. According to the first, the metallothermic reactions of reduction of elements from their oxides occur during the thermochemical treatment itself. The heat released during the exothermic reactions is used for a momentary rise in the temperature of the powder mixture so as to accelerate diffusion saturation [121]. Small amounts of aluminum oxide or other stable oxides are added to the powder mixture to prevent sintering. When it is necessary to reduce the temperature of the reaction zone during the reduction of oxides, some oxides, in larger quantities, are added to the impregnating mixture. They absorb a part of the heat and prevent fusion of the workpiece. Similarly, when powders of pure metals or ferroalloys are used for impregnation, small amounts of activators, (NH_4Cl, AlF_3, NaF, etc.), added to the charge, interact with the impregnating elements and form an active gaseous phase at the process temperature.

In the second variation of thermochemical treatment, metallothermic reactions are used only for preparation of impregnating mixtures. Mixtures of the powder oxides of impregnating elements with inert addition and halide activators are heated to promote the reaction for the reduction of oxides. They are then cooled to room temperature and used for thermochemical treatment.

The thermodynamic feasibility of reduction of oxides can be found from the change in free-energy of the reduction process.

High negative values of ΔG^0 indicate the possibility of rapid occurrence of the reaction and high positive values indicate the impossibility of the reaction under any conditions. At moderate positive or negative values of ΔG^0, the occurrence of the process in the forward as well as in the backward direction is possible. It is necessary to create favorable conditions for the reaction to take place in the required direction (appropriate temperature, pressure, withdrawal of the products of reaction from the reaction zone, etc.).

The temperature dependence of the free-energy change in reactions for the reduction of oxides of various elements by aluminum [119], silicon [122] and calcium silicide, $CaSi_2$ (which is close in composition to normally produced alloys of calcium and silicon in industry) are given in Figs. 12–14.

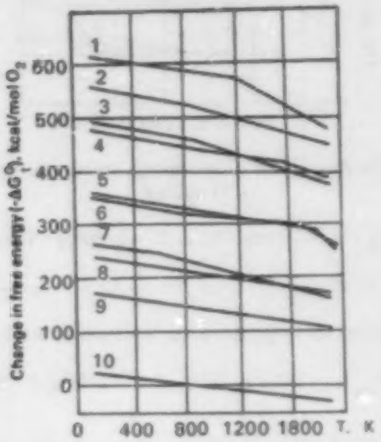

Fig. 12. Temperature dependence of free-energy change during reduction of oxides by aluminum:

1—$\frac{2}{3}MoO_3+\frac{4}{3}Al=\frac{2}{3}Mo+\frac{2}{3}Al_2O_3$; *2*—$\frac{2}{3}WO_3+\frac{4}{3}Al=\frac{2}{3}W+\frac{2}{3}Al_2O_3$; *3*—$\frac{2}{5}V_2O_5+\frac{4}{3}Al=\frac{4}{5}V+\frac{2}{3}Al_2O_3$; *4*—$\frac{2}{3}Mn_2O_3+\frac{4}{3}Al=\frac{4}{3}Mn+\frac{2}{3}Al_2O_3$; *5*—$\frac{2}{3}Cr_2O_3+\frac{4}{3}Al=\frac{4}{3}Cr+\frac{2}{3}Al_2O_3$; *6*—$\frac{2}{5}Nb_2O_5+\frac{4}{3}Al=\frac{4}{5}Nb+\frac{2}{3}Al_2O_3$; *7*—$\frac{2}{3}B_2O_3+\frac{4}{3}Al=\frac{4}{3}B+\frac{2}{3}Al_2O_3$; *8*—$SiO_2+\frac{4}{3}Al=Si+\frac{2}{3}Al_2O_3$; *9*—$TiO_2+\frac{4}{3}Al=Ti+\frac{2}{3}Al_2O_3$; *10*—$ZrO_2+\frac{4}{3}Al=Zr+\frac{2}{3}Al_2O_3$.

It can be seen from Fig. 12 that, in the temperature range employed in thermochemical treatments, aluminum easily reduces oxides of molybdenum, tungsten, vanadium, chromium, niobium, manganese, boron, silicon and titanium while the reduction of oxide of zirconium is considerably difficult.

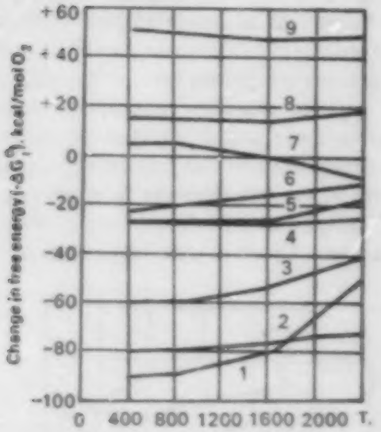

Fig. 13. Temperature dependence of free-energy change during reduction of oxides by silicon:

$1-\frac{2}{3}MoO_3+Si=\frac{2}{3}Mo+SiO_2$; $2-\frac{2}{3}WO_3+Si=\frac{2}{3}W+SiO_2$;
$3-\frac{2}{5}V_2O_5+Si=\frac{4}{5}V+SiO_2$; $4-\frac{2}{3}Cr_2O_3+Si=\frac{4}{3}Cr+SiO_2$;
$5-\frac{2}{5}Nb_2O_5+Si=\frac{4}{5}Nb+SiO_2$; $6-2MnO+Si=2Mn+SiO_2$;
$7-\frac{2}{3}B_2O_3+Si=\frac{4}{3}B+SiO_2$; $8-TiO_2+Si=Ti+SiO_2$; $9-ZrO_2+Si=Zr+SiO_2$.

The powder mixture charge for two-component impregnation must contain oxides of the impregnating elements and aluminum, the quantity of which should be less than that theoretically required for reduction of the oxides (diffusion coating by elements produced by the reduction of oxides).

When an excess of aluminum exists in a charge containing one or two oxides of impregnating elements, simultaneous impregnation by two or three components can be expected to take place, one of which will be aluminum.

Two-component coatings of the type Me_1+Me_2 (Cr+Si, Cr+Ti, V+Si, Zr+Si, Ti+Si, etc.), Me+Al (Cr+Al, Ti+Al, Si+Al, Zr+Al, etc.) and, similarly, three-component coatings of the type Me_1+Me_2+Al (Cr+Ti+Al, Cr+B+Al, B+Ti+Al, etc.) [102–109] on the surfaces of steels and alloys were obtained by the use of aluminum as a reducing agent for the oxides.

At normal temperatures of thermochemical treatment silicon is a sufficiently strong reducing agent and can reduce many oxides to elements (Fig. 13). It easily reduces oxides such as MoO_3, WO_3, V_2O_5, Cr_2O_3, Nb_2O_5, MnO, etc.

Reduction of boric anhydride by silicon takes place only under special conditions. *The high positive values of free-energy change in the reaction for* reduction of TiO_2 and ZrO_2 by silicon indicates a low probability of their reduction even under special conditions.

Reactions of silicothermic reduction of oxides are less exothermic as compared to aluminothermic reactions. Therefore, the basic function of inert additions during thermochemical treatment in silicothermic mixtures is to prevent sintering. Not only silicon but, possibly, ferrosilicon can also be used as reducing agents. As in the case of aluminothermic mixtures, here also, it is possible to obtain one- or multicomponent diffusion coatings on metals and alloys. The formation of two-component diffusion layers by Mo + Si, W + Si, Cr + Si and B + Si is of considerable interest.

A comparison of temperature dependences of free-energy exchanges in the reactions for the reduction of oxides by calcium disilicide, $CaSi_2$, aluminum and silicon (see Figs. 12–14) shows that $CaSi_2$ is a much stronger reducing agent than silicon, but it is weaker than aluminum in this respect. At the treatment temperatures, $CaSi_2$ can easily reduce the following oxides; MoO_3, WO_3, Cr_2O_3 and with a slightly lower intensity, it can also reduce B_2O_3 (see Fig. 14).

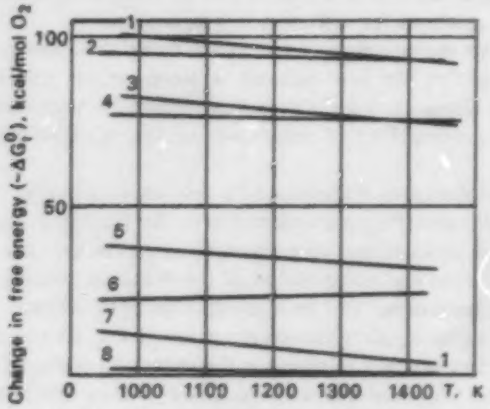

Fig. 14. Temperature dependence of free-energy change during reduction of oxides by calcium disilicide:

$1-\frac{2}{3}MoO_3+2CaSi_2=\frac{2}{3}Mo+4Si+2CaO$; $2-\frac{2}{3}MoO_3+\frac{2}{5}CaSi_2=\frac{2}{3}Mo+\frac{2}{3}CaO+\frac{4}{5}SiO_2$; $3-\frac{2}{3}WO_3+2CaSi_2=\frac{2}{3}W+4Si+2CaO$; $4-\frac{2}{3}WO_3+\frac{2}{5}CaSi_2=\frac{2}{3}W+\frac{2}{5}CaO+\frac{4}{5}SiO_2$; $5-\frac{2}{3}Cr_2O_3+2CaSi_2=\frac{4}{3}Cr+4Si+2CaO$; $6-\frac{2}{3}Cr_2O_3+\frac{2}{5}CaSi_2=\frac{4}{3}Cr+\frac{2}{5}CaO+\frac{4}{5}SiO_2$; $7-\frac{2}{3}B_2O_3+2CaSi_2=\frac{4}{3}B+4Si+2CaO$; $8-\frac{2}{3}B_2O_3+\frac{2}{5}CaSi_2=\frac{4}{3}B+\frac{2}{5}CaO+\frac{4}{6}SiO_2$.

Somewhat higher negative values of ΔG^0_T for the reactions 1, 3, 5 and 7 as compared to those for the reactions 2, 4, 6 and 8 indicate that during reduction of oxides by calcium disilicide, the reactions during which only calcium is oxidized have a thermodynamically higher probability. Such reactions can lead to the formation of two-component diffusion coatings, such as Mo+Si, W+Si, Cr+Si, B+Si.

Two-component coatings can also be formed, if the addition of calcium disilicide in the mixture is more than necessary for reduction of the oxides. Increasing the temperature up to 1400–1500 K renders the reactions 1 and 2, 3 and 4, 5 and 6, 7 and 8 equiprobable. In addition the probability of occurrence of the reactions 2, 4, 6 and 8 may increase due to the formation of silicates of calcium in the mixture. Thus, at a moderate concentration of calcium disilicide in the mixture, a one-component diffusion coating can be expected; an increase in the concentration of calcium disilicide in the mixture should facilitate the formation of two-component diffusion layers and an increase of silicon content in them. Borided, borosilicided, chromized and chromosiliconized layers on iron and steel have been obtained using boric anhydride, and calcium silicide and oxides of chromium, and calcium-silicide based powder mixtures for diffusion impregnation.

According to the principle of successive transformation given by Baikov [110], higher oxides are first reduced to lower oxides and then the latter are reduced to elements. Lower oxides are generally more stable than higher oxides and the probability of occurrence of the reaction depends on their reducibility.

During simultaneous reduction of a few oxides, oxides with maximum dissociation pressure (P_{O_2}) are reduced first. By changing the concentration of oxides in the mixture and, consequently, the pressure, the reducibility of the oxides and chemical composition of the diffusion coating formed on the surface of the base metal can be altered. During the course of reduction of oxides with a higher equilibrium oxygen pressure P_{O_2}, its concentration in the impregnating mixture falls resulting in the reduction of P_{O_2} of this oxide and renders possible the simultaneous reduction of two or more oxides.

As shown by the investigation conducted by the authors activators (NH_4Cl, AlF_3, NaF, etc.), the dissociation products of which, at treatment temperatures, form gaseous compounds with the impregnating elements, not only accelerate the thermochemical treatment in powder mixtures but also significantly influence the course of the aluminothermic reduction of oxides.

Introduction of 3 to 5% AlF_3 in the charge for diffusion chromizing (80% Cr_2O_3 and 20% Al) and 2–3% NH_4Cl in the charge for chromosiliconizing (68% Cr_2O_3, 12% SiO_2 and 20% Al) significantly reduces the onset temperature of the aluminothermic reaction (Fig. 15). This is probably related to breaking of the oxide film on the aluminum resulting in a catalytically active

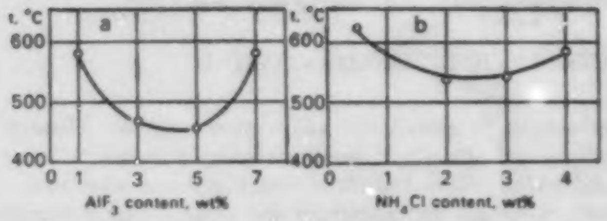

Fig. 15. Effect of halide additions in chromizing mixtures on temperatures of onset of aluminothermic reaction.

surface of aluminum. The possibility of reduction of Al_2O_3 by halides has been experimentally demonstrated by Dubinin [101] who has established that, during chromizing in powder mixtures of chromium (a ferrochrome), oxide of aluminum and halide activators, together with chromium, aluminum is also present in the diffusion layers.

Inert additions which are made to metallothermic (impregnating) mixtures to reduce the rise in temperature during the process of reduction, to prevent fusion of the workpiece and prevent sintering of the mixture, also increase the onset temperature of the reduction. The effect of an Al_2O_3 addition of the mixture for chromosiliconizing (68% Cr_2O_3, 12% SiO_2 and 20% Al) on the temperature of the onset and end of the reduction reaction is shown in Fig. 16. Without an Al_2O_3 addition the process of reduction occurs at such a fast rate that it is not possible to distinguish between the initial and the final temperatures of reduction of Cr_2O_3 and SiO_2, respectively, due to the high response time of the recording potentiometer. With the introduction of inert

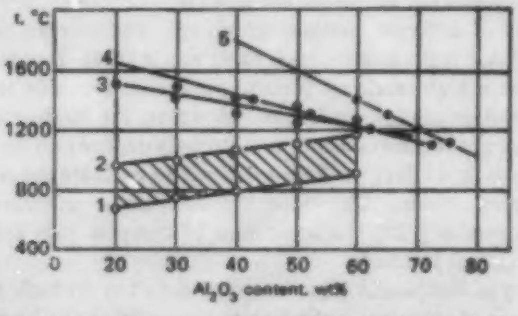

Fig. 16. Effect of Al_2O_3 addition on temperature of onset and end of reactions in reduction of oxides during chromosiliconizing:

1 and 2—Temperatures at beginning of reduction of oxide of chromium and dioxide of silicon, respectively; 3 and 4—Temperatures at end of these reactions; 5—Theoretical temperature at end of reaction (NH_4Cl—2%).

additions, the sequential nature of the reduction of oxides becomes evident: first the less stable Cr_2O_3 and then the more stable SiO_2.

2. ELECTROLYTIC DIFFUSION COATING

Diffusion coating of metals and alloys either with one element (carbon, boron, silicon and others) or, simultaneously, with two or more elements (boron and silicon, boron and chromium, boron and aluminum, chromium and silicon, chromium and aluminum and other similar groupings) can be carried out by electrolysis of fused salts or oxides.

For thermochemical treatment mainly such compounds are used (borates, phosphates, silicates, tungstates, etc.) which can be assumed to be melts of two or more oxides. Therefore, it will be proper to examine the thermodynamic and mechanism of the oxide systems used in electrolytic processes.

Faraday's law is equally applicable to cathodic as well as anodic processes during electrolysis of widely different oxide systems [124] (exceptions are melts rich in oxides of iron, cobalt and other transition elements which are 'ionic-electronic' conductors). The order of deposition of elements on the cathode, on slowly increasing the applied voltage, qualitatively agrees with the stability of the oxides, i.e. it depends on the extent of variation in the free energy in decomposition of the oxides.

Processes taking place during electrolysis of fused oxides can be analyzed with the help of statistical thermodynamics of ionic solutions, developed by Kozheurov [125] for metallurgical slags. The objections raised in the literature [126] against such an analysis of the electrolytic process of thermochemical treatment are baseless. The main argument against such an approach is the assertion that the impregnating element exists in borates, silicates and other oxide systems not as free atomic ions (B^{3+}, Si^{4+}, Al^{3+}, P^{5+} and others), but as a part of different complex groupings. The modern concept of the structure of fused melts and oxides is explained in [124]. Borates and silicates certainly have a high tendency toward polymerization, due to which fairly complex spatial groupings are formed. However, the binding energy within grouping does not remain constant and strongly depends on the composition of the melt which, in fact, makes it difficult to evaluate the energy of melts of different compositions. Therefore, thermodynamic calculations, as indicated by Kozheurov [125], the separation of complex ions and other complex particles is not justified.

The theory of Kozheurov takes into consideration the basic characteristics of the structure of ionic melts, the diverse character of the boriding between structural elements and the resultant nonadditivity of energy and leads to good agreement between the theoretical data evaluated for the most important metallurgical equilibriums and the experimental values.

A statistical thermodynamic approach to the ionic melts was used by the authors for explaining the mechanisms of boriding and siliconizing [76, 121].

The method of calculating the difference between the dissociation potentials of oxides in two-component oxide systems described in [76, 121] can also be used for the processes taking place in the melts of more complex oxide systems during electrolytic impregnation of metals and alloys, simultaneously with two or more elements.

The following general equations were obtained for calculation of differences in the decomposition potential of oxides, in a three-component oxide system:

$$E_1-E_2=\frac{1}{z_1z_2F}\left[z_2\Delta G_1^0-z_1\Delta G_2^0+RT\ln\frac{x_2^{z_1v_2}}{x_1^{z_2v_1}}+Q_{12}(z_1v_2x_1-z_2v_1x_2)\right.$$
$$\left.+x_3(z_1v_2Q_{23}-z_2v_1Q_{13})-(x_1x_2Q_{12}+x_1x_3Q_{13}+x_2x_3Q_{23})(z_1v_2-z_2v_1)\right], \quad (1)$$

$$E_2-E_3=\frac{1}{z_2z_3F}\left[z_3\Delta G_2^0-z_2\Delta G_3^0+RT\ln\frac{x_3^{z_2v_3}}{x_2^{z_3v_2}}+Q_{23}(z_2v_3x_2-z_3v_2x_3)\right.$$
$$\left.+x_1(z_2v_3Q_{23}-z_3v_2Q_{12})-(x_1x_2Q_{12}+x_1x_3Q_{13}+x_2x_3Q_{23})(z_2v_3-z_3v_2)\right], \quad (2)$$

where E_1, E_2, and E_3 are the decomposition potentials of the oxides in the given system; z_1, z_2 and z_3 the number of electrons participating in the elementary act of dissociation of the first, second and third oxide, respectively; v_1, v_2 and v_3 the number of cations, comprising the molecules of the components (oxides); x_1, x_2 and x_3 the ionic fractions of cations of components one, two and three, respectively, in the melt; ΔG_1^0, ΔG_2^0 and ΔG_3^0 the standard free-energy change for decomposition of the oxides; and Q_{12}, Q_{13} and Q_{23} the energy of mixing corresponding to the first and second, first and third, and second and third oxides, respectively.

Results of calculations of the difference in potentials for decomposition of oxides in melts of the Na_2O–B_2O_3–SiO_2, Na_2O–Cr_2O_3–SiO_2 and Na_2O–B_2O_3–Fe_2O_3 systems are given as an example of the application of the above relations. Melts of the first two systems are used in electrolytic borosiliconizing and chromosiliconizing. The last system was studied with a view to understand the phenomena taking place during electrolytic boriding in industrial baths in metallic crucibles, where contamination of borax by the oxides of iron cannot be avoided.

For calculations, the necessary values of ΔG_i^0 at the assumed temperature of electrolysis were obtained from [127], the values of Q_{ij} of oxides were calculated from the heats of formation of oxides or from the corresponding phase diagrams. Values of heats of mixing of oxides are given in Table 1.

Table 1

System	Heat of mixing of oxide kcal/mol
Na_2O–SiO_2	−85.0
Na_2O–B_2O_3	−60.0
Na_2O–Cr_2O_3	−96.5
Na_2O–Fe_2O_3	4.7
B_2O_3–SiO_2	−94.0
Cr_2O_3–SiO_2	−36.5
B_2O_3–Fe_2O_3	−100.0

The results of calculations are given in Tables 2–4.

It can be seen from Table 2 that a variation in the composition of the electrolyte for borosiliconization results in a change of stability of the oxides comprising the melts. Electrochemical reduction of ions of sodium, silicon and boron at the cathode is thermodynamically feasible in all the melts, whereas chemical reduction of boron ions by sodium atoms, formed electrochemically at the cathode, is possible only in borax melts with 10 to 20% of sodium monosilicate and is impossible with silicon. In borax melts with 10–70% of Na_2SiO_3, ions of boron can be discharged at the cathode at a lower voltage in the bath and, consequently, at a lower current density. In melts with 10% of borax, ions of silicon may be liberated at the cathode at a current density lower than that for boron.

Thus, variations in the composition of the borax-sodium silicate melt and parameters of electrolysis can result in the formation of siliconized borided and borosiliconized diffusion layers.

The sequence of the processes occurring during electrolysis of borax-sodium monosilicate melts (plotted according to calculations), the phases formed at different bath compositions and voltages during electrolytic borosiliconizing are given in Figs. 17 and 18, respectively. Lines in the plot (Fig. 17) represent the variation in the decomposition potential of the oxides Na_2O, B_2O_3, SiO_2 as a function of composition of the electrolyte. In the plot representing the phases formed at different compositions of the bath and voltage across the electrolytic cell, only those points are given which correspond to electrolysis at 1050°C.

Thus, the experimental equilibrium diagram for borosiliconizing fully supports the chart, schematic mechanism of the processes occurring during electrolytic borosiliconizing.

During chromosiliconizing (Table 3) in an electrolyte containing 5 to 25% Cr_2O_3, ions of silicon are more electropositive than ions of chromium and sodium. With the increase in Cr_2O_3 content in a sodium monosilicate melt

Table 2

Melt composition, mol. %		x_1	x_2	x_3	$E_{Na_2O}-E_{B_2O_3}$, V		$E_{B_2O_3}-E_{SiO_2}$, V	
$Na_2B_4O_7$	Na_2SiO_3				1200 K	1300 K	1200 K	1300 K
90	10	0.35	0.63	0.02	0.62	0.51	−0.76	−0.73
70	30	0.39	0.55	0.06	0.33	0.22	−0.58	−0.55
50	50	0.45	0.45	0.10	0.06	−0.05	−0.39	−0.37
30	70	0.51	0.31	0.18	−0.27	−0.38	−0.09	−0.11
10	90	0.61	0.12	0.27	−0.66	−0.76	0.24	0.26

Table 3

Melt composition, mol. %		x_1	x_2	x_3	$E_{Na_2O}-E_{Cr_2O_3}$, V		$E_{Cr_2O_3}-E_{Si_2O_3}$*, V	
Na_2SiO_3	Cr_2O_3				1300 K	1400 K	1300 K	1400 K
95	5	0.64	0.04	0.32	0.03	−0.08	0.25	0.26
90	10	0.62	0.07	0.31	0.17	0.07	0.20	0.20
85	15	0.60	0.10	0.30	0.31	0.22	0.15	0.16
80	20	0.57	0.14	0.29	0.50	0.41	0.10	0.10
75	25	0.55	0.18	0.27	0.67	0.57	0.04	0.05

*Most likely an error in the original, should read SiO_2—Translator.

Table 4

$Na_2B_4O_7$		Fe_2O_3					$E_{Na_2O}-E_{B_2O_3}$, V	$E_{B_2O_3}-E_{Fe_2O_3}$, V
mol. %	wt. %	mol. %	wt. %	x_1	x_2	x_3	1200 K	1200 K
100	100	0	0	0.333	0.667	0	0.187	—
98.7	99	1.3	1	0.329	0.658	0.013	0.141	−0.116
97.5	98	2.5	2	0.325	0.650	0.025	0.100	−0.053
96.2	97	3.8	3	0.321	0.641	0.038	0.043	0.010
93.6	95	6.4	5	0.312	0.624	0.064	−0.049	0.068

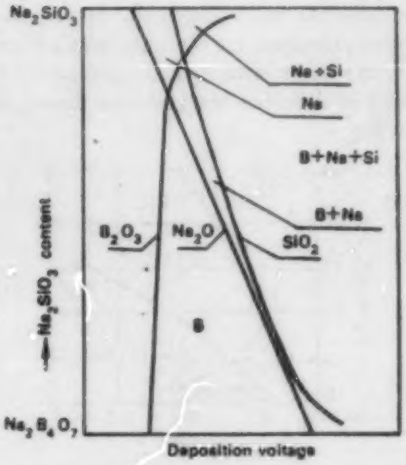
Na₂SiO₃
Na+Si
Na
B+Na+Si
B+Na
SiO₂
B₂O₃
Na₂O
B
→ Na₂SiO₃ content
Na₂B₄O₇
Deposition voltage

Fig. 17. Phases formed at different compositions of bath and voltage across electrodes, during electrolysis of borax-sodium monosilicate melts.

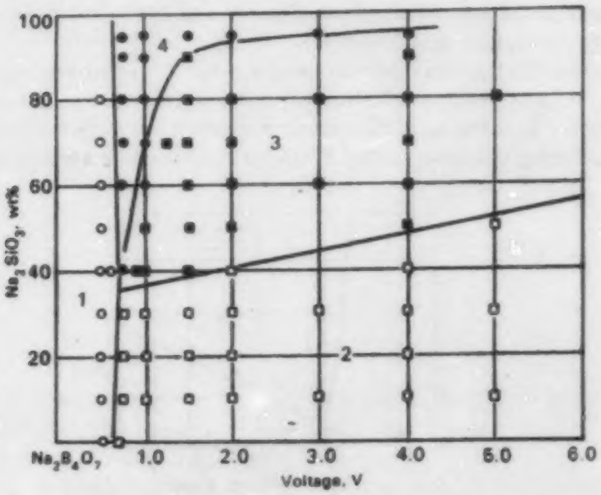

Fig. 18. Phases formed at different compositions of bath and voltage across electrodes during electrolytic borosiliconizing:

1—no layer formation; 2—boriding; 3—borosiliconizing; 4—siliconizing.

up to 25%, the difference between the decomposition potentials of Cr_2O_3 and Na_2O increases (in absolute value), whereas for Cr_2O_3 and SiO_2 it falls, practically to zero. Ions of sodium are more electronegative than ions of chromium and silicon in the entire investigated concentration range of Cr_2O_3. Regions of deposition of different types of ions during electrochemical reactions are shown in Fig. 19.

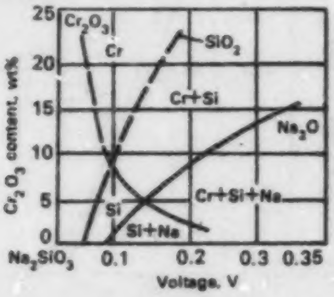

Fig. 19. Processes occurring during electrolysis of sodium monosilicate–chromium oxide–sodium chloride melt.

Hypothetical plots of phases formed at different current densities and bath compositions, synthesized according to thermodynamic calculations and experimental data are shown in Figs. 19 and 20 (melt: Na_2SiO_3 + Cr_2O_3 + 15–20% NaCl, base metal steel 45).

It is observed that the theoretical and experimental data are in good agreement. Qualitative differences are, most probably, due to the introduction of sodium chloride in the melt, the presence of which has been taken into consideration during calculations. Similarly, good qualitative agreement between

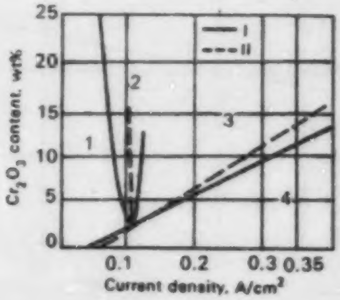

Fig. 20. Phases formed during electrolytic chromosiliconizing of steel 45: 1—no layer formation; 2—chromizing; 3—chromosiliconizing; 4—siliconizing. (I—1100°C, τ=3 h; II—1000°C, τ=3 h).

theoretical and experimental data was obtained for electrolysis of melts of Na_2O–Cr_2O_3–B_2O_3 [77] and Na_2O–B_2O_3–Al_2O_3 [128] systems.

The study of Na_2O–B_2O_3–Fe_2O_3 and Na_2O–B_2O_3–NiO systems was of special interest from the practical as well as the theoretical point of view. From the practical aspect, a correct understanding of the process taking place during electrolysis of the aforementioned system is important for estimating the effect of contamination of borax by oxides of iron and nickel on the boriding process in metallic crucibles and to ensure effective refining of the melt during electrolytic boriding in a bath. The theoretical interest is based on the fact that oxides of iron and nickel, on dissolution in borax, make it a mixed conductor and lead to considerable anomalies in its behavior as a fused electrolyte.

On the basis of these calculations (see Table 4), a plot of the variation of decomposition of potential of oxides in $Na_2B_4O_7$–Fe_2O_3 system (Fig. 21) [129] has been prepared. As can be seen from this plot, variations in the concentration of Fe_2O_3 in the borax melt and parameters of electrolysis can lead to deposition of ions of boron, boron and sodium, boron and iron and formation of a boride diffusion layer, to the presence of ions of iron or iron and sodium at the cathode and interaction of atomic iron with the cathode material.

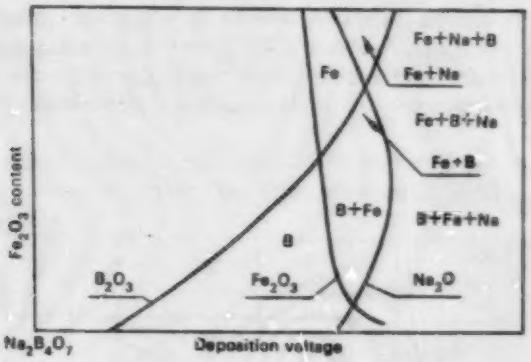

Fig. 21. Variation of decomposition potential of oxides in a borax-ferric oxide system.

As indicated in [130], a borax melt, in which metal oxides are dissolved, may contain metal atoms and their borides after electrolysis. It may, therefore, be assumed that, in a melt of borax and ferric oxide, iron and borides of iron may exist after electrolysis.

Results of investigations on the effect of Fe_2O_3 and NiO, in a borax melt on the thickness of the diffusion layer are reproduced in Fig. 22. At a current density of 0.2 A/cm^2, which is generally used during electrolytic boriding, an

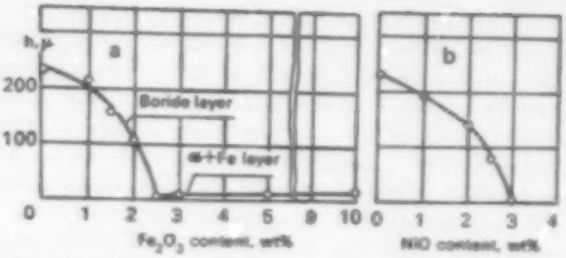

Fig. 22. Effect of concentration of oxides of (a) iron and (b) nickel in a borax melt on thickness of the diffusion layer ($t=950$°C, $\tau=2$ h, current density $=0.2$ A/cm^2).

increase in the concentration of Fe_2O_3 (up to 2.5 wt.%) and NiO (up to 3 wt.%) leads to a sharp reduction in the thickness of the borided layer on steel 40. Electrolysis does not produce a borided layer on the surface of the specimen if the concentration of Fe_2O_3 and NiO in the melt is further increased.

The effect of current density on thickness of the borided layer for different bath compositions (borax + ferric oxide) is shown in Fig. 23. With an increase in Fe_2O_3 content in the melt, the minimum current density at which a boride layer is formed on the surface of the specimen cathode increases from 0.02 A/cm^2 for pure borax to 0.47 A/cm^2 for a borax melt with 5% Fe_2O_3, and the maximum thickness of a borided layer which can be obtained in an identical temperature-time cycle of surface impregnation, is significantly reduced.

The variation in structure of diffusion layers formed during electrolysis of a borax + ferric oxide melt, with the melt composition and current

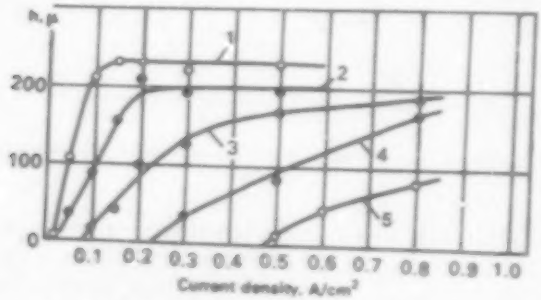

Fig. 23. Effect of current density on thickness of borided layer at different bath compositions (borax + ferric oxide system):

1—borax; 2—borax + 1% Fe_2O_3; 3—borax + 2% Fe_2O_3; 4—borax + 3% Fe_2O_3; 5—borax + 5% Fe_2O_3.

density during electrolysis is shown in Fig. 24. Variation in these parameters leads to the formation of diffusion layers of boride or α-Fe layers on the surface of the steel cathode.

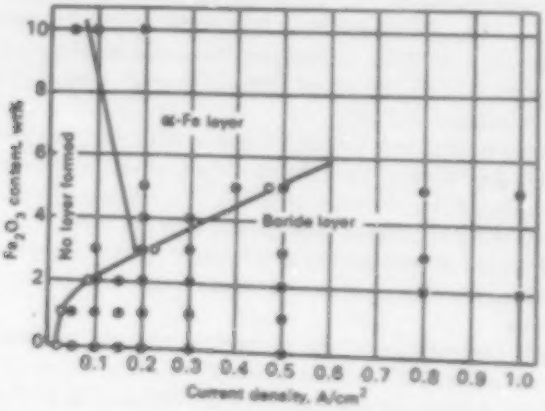

Fig. 24. Variation in structure of diffusion layers with ferric oxide content in fused borax and with current density. Steel 40, $t = 950$°C, $\tau = 2$ h.

In melts containing up to 3% of Fe_2O_3, only diffusion layers of boride are formed at the cathode. Further, with 3 to 5% concentrations of Fe_2O_3 in melts, either a layer of iron (α-Fe) or boride (at higher current densities) is formed on a steel cathode.

In order to ascertain the mechanism of the processes occurring during electrolysis of melts of borax with Fe_2O_3, after electrolysis at 950°C for 2 h at constant current densities of 0.1, 0.4 and 0.6 A/cm², the portion of the electrolyte (borax with 5% Fe_2O_3) insoluble in water, was subjected to phase analysis by an x-ray diffraction method. From the phase diagram (Fig. 24) it was observed that after electrolyzing at constant current density of 0.1 A/cm², the diffusion layer on the cathode could not be detected by metallography. On the cathode surface an α-Fe layer was formed at a current density of 0.4 A/cm², while at 0.6 A/cm² a boride layer was formed.

After electrolysis, the bath was cooled, a sample was drawn and dissolved in boiling water and filtered through a folded filter paper. The residue was dried, subjected to magnetic separation and the magnetic fraction was subjected to x-ray diffraction analysis. The x-ray diffraction pattern was obtained on an URS-50IM using iron K_α-radiation at a counter rotation rate of 4°/min and a chart speed of 2400 mm/h. The set of slits used was ≪0.1, 1.0, 0.1≫.

After electrolysis at a current density of 0.1 A/cm² metallic iron was detected in the cooled melt, while at 0.4 and 0.6 A/cm² both iron and borides of iron, FeB and Fe_2B, were found. Most probably, at a current density of 0.1 A/cm² Fe_2O_3 may already have decomposed. Possibly, at the cathode, reduction of the ionic to atomic iron takes place in steps. Atoms of iron partly go into the melt and are partly retained at the surface of the cathode. An equilibrium $Fe_{cathode} \gtrless Fe_{melt}$ is established. Iron, which goes into the melt, can be easily detected by x-ray diffusion analysis of the magnetic fraction of the residue. Iron which is deposited at the cathode in small quantities is not found in the form of isolated particles.

At a current density of 0.4 A/cm² during electrolysis, evidently both iron and boron are deposited on the cathode. Most of the boron reduced at the cathode forms borides in the cathode space. The amount of iron deposited at the cathode is sufficient for the formation of an α–Fe layer.

Electrolysis at a current density of 0.6 A/cm² further increases the amount of boron deposited at the cathode and results in the formation of a diffusion layer of boride.

Thus, the composition of the electrolyte and the process parameters govern the variation in the ratio of iron and boron deposited on the cathode which, in turn, determines the nature of the diffusion layer formed on the electrode.

The experimental data quoted avove confirms that the assumption made for the thermodynamic calculations are valid and the correlations obtained are useful for an approximate estimate of the zones of formation of one- or multicomponent diffusion coatings during the electrolytic process in thermochemical treatment.

The good agreement of the calculated and experimental data (significant quantitative deviations were observed only in the Na_2O–SiO_2–Cr_2O_3 system) also confirms the correctness of the aforementioned assumptions regarding the mechanism of electrolytic processes.

On the basis of investigations carried out the following recommendations for producing electrolytic diffusion coatings can be made:

1. A two-component diffusion layer of definite thickness, structure and chemical composition can be obtained by electrolysis of melts of precisely known compositions at predetermined values of the parameters of electrolysis (current density, temperature and time).

2. During electrolytic diffusion coating of metals and alloys, simultaneously with two elements, the variation in the composition of the melt should be taken into account. It may lead to a variation in the ratio of elements being deposited on the cathode and, consequently, change the structure and chemical composition of the diffusion layer. In order to provide stability to electrolytic process, it is necessary to periodically correct the composition of the bath and strictly maintain the prescribed parameters of electrolysis.

3. During electrolytic diffusion coating in metal crucibles, it is necessary, as far as possible, to control contamination of the melt by oxides of iron,

nickel and chromium used as a general cathodic protection for the crucible and for protection of crucible accessories at the melt-furnace atmosphere interface.

3. LIQUID ELECTROLESS PROCESS OF DIFFUSION COATING

The process of electroless diffusion saturation in the melts of salts and oxides containing reducing materials is used for the production of carbonitrided, borided, silicided, chromized, borosilicided, borochromized, chromosilicided and other one- or two-component diffusion layers. In these cases active atoms of impregnating elements are continuously formed in the bath as a result of an electrochemical interaction between the reducing agent and the component being impregnated.

Earlier investigations on electrochemical treatment in liquid diffusion coating processes has been reported in the works of Illushchenko [131, 132] and Lyakhovich and Dolmanov [133, 134].

The phenomenon of spontaneous transport of electronegative metals with the formation of alloys in fused salt electrolytes has been discussed in detail in [131, 132]. On placing a metal (Me_1) and its alloy (Me_1–Me_2) (Me_1 being more electronegative as compared to Me_2) in the melt an equilibrium is established between the metal (alloy) and its salt dissolved in the melt.

$$(m-n)\,Me_1+nMe_1^{m+}\rightleftarrows mMe_1^{n+},$$

where Me_1^{m+} are the ions of impregnating elements with a higher valency; and Me_1^{n+} the ions of the same elements but with a lower valency (subions).

The equilibrium constant for this reaction can be determined from the activities of the components

$$K=\frac{(a_{Me_1^{n+}})^m}{(a_{Me_1^{m+}})^n\,(a_{Me_1})^{m-n}}.$$

As the activity of the electronegative metal in the alloy is less than that in the pure metal, the activity of the ions of higher valency is lower in the vicinity of the pure metal electrode, than near the alloy. The tendency to equalize the activity of ions near the electrodes by diffusion and convective transport leads to dissolution of the electrode of the pure metal

$$(m-n)\,Me_1+nMe_1^{m+}\rightleftarrows mMe_1^{n+}$$

and enrichment of the alloy by them

$$xMe_1\,yMe_2+m\,Me_1^{n+}\rightarrow[x\,(m-n)\,Me_1\,y\,Me_2+n\,Me_1^{m+}].$$

The rate of transport sharply increases with a reduction in the distance between the electrodes, for example, on immersing an alloy in a powder of the electronegative metal present in the alloy.

The maximum rate of reaction is reached when the electronegative metal and its alloy are in contact with each other, and a galvanic cell of the following type is established:

Me_1	Electrolyte, containing	$Me_1 + Me_2$ (alloy)
(Anode)	Me_1 ions	(cathode)

When powder materials are used as reducing agent, anodic activators according to the terminology of [133, 134], there is almost constant contact between the powder and the material being impregnated and a study of the principles of alloy formation in fused electrolytes, in fact, involves studying the functioning of the galvanic cell described above.

Basic principles of the functioning of similar types of galvanic cells have been discussed in detail in [121] and are, therefore, not discussed here.

Similar mechanisms of formation of diffusion coatings have also been established when oxide systems were employed as eletrolytes [133, 134]. It has been shown that any anode material, which has a negative electrode potential in a given electrolyte with respect to the impregnating metal and a sufficiently low polarizability, can be used for reducing the oxide of the substrate metal, resulting in the formation of active atoms. Only such phases which are more electronegative than the reducing agent can be formed on the surface of the metal being impregnated.

The process of diffusion impregnation in such a case takes place mainly as a result of the functioning of the following galvanic cell:

Component	Electrolyte, containing ions	Reducer
(cathode)	of impregnating element	(anode)

Substitution of the powder of an impregnating element by any other material which is electronegative with respect to the substrate metal and which can reduce the oxide of the impregnating element, does not introduce any radical change in the material-transport mechanism as the process of alloying (formation of a diffusion coating) in this case also takes place due to the formation of ions of different (lower and higher) valencies.

The effectiveness of the working of a galvanic cell depends on the difference between the electrode potentials of the metal and the reducer, as well as on the aggregate ohmic resistance of the galvanic cell. The process of surface alloying of the component proceeds till the potential of the surface being impregnated is positive as compared to the reducer.

For comparison of oxidizing—reducing activities of materials in any electrolyte, the electrochemical potential series is used where every subsequent element (from left to right) has a higher positive potential than the next one.

The electrochemical potential series for some alloys, which can be used for multicomponent diffusion coating is given in Fig. 25.

As in the case of electrolytic impregnation, the chemical composition and

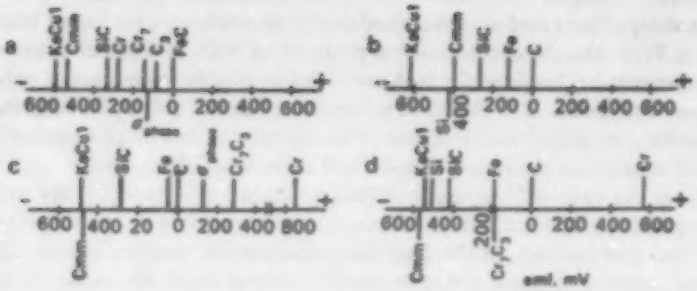

Fig. 25. Electrode potentials of some materials in melts:

a—borax at 950°C; b—40% borax + 40% chromic oxide + calcium fluoride; c—70% eutectic of the fluorides of calcium and sodium + 30% chromic oxide; d—70% fluoride eutectic + 30% silicon dioxide; e—60% fluoride eutectic + 16% chromic oxide + 24% silicon dioxide; reference electrode—graphite, $t = 1000°C$.

structure of diffusion layers obtained during electroless liquid impregnation depends on the composition of the oxide or salt melt which determines the decomposition potential of the oxides or salts. Therefore, Eqs. (1) and (2) in Chapter II, derived for evaluating the differences in the decomposition potential of the oxides in a three-component oxide system during electrochemical impregnation, can also be used for investigation of electroless liquid impregnation processes.

Variation in the composition of the electrolyte containing cations of the impregnating elements for a given reducer can lead to the formation of one- or two-component diffusion layers of different chemical compositions. At a constant composition of the electrolyte, an increase in the amount of reducer should not make any change in the type of diffusion layer. Variation can be expected only in the depth of the layer and concentration of impregnating elements. Any change in the type of diffusion layer at a constant composition of the electrolyte can take place only if one reducer is replaced by another.

Thus, for example, in borax melts containing oxides of chromium, where a 10 wt.% of sodium fluoride was added to reduce the viscosity, at a constant concentration of the reducer (10% calcium silicide of CaSi I grade) different diffusion coatings were obtained on iron and plain carbon steels such as boride layers (at a chromic-acid concentration in the bath of up to 5 wt.%), chromized layers (at a chromic-oxide concentration above 12–15 wt.%) and borochromized layers (at 6 to 12 wt.% of chromic acid).

In melts containing 40% Cr_2O_3, variation in the calcium-silicide content from 3 to 40% did not lead to any change in the type of diffusion layer formed at the surface of iron and steels. Only chromized diffusion layers were obtained. At higher concentrations of calcium silicide the viscosity of the melts sharply increased and thus rendered them unsuitable for liquid impregnation. Probably, the decomposition potential of B_2O_3 in melts of borax with high chromic-oxide content is high and calcium silicide cannot act as reducer of boric anhydride. The electrode potential of calcium silicide in such melts, is, possibly, more positive than that of borides of iron and more negative than a solid solution of chromium in α–Fe and carbides of chromium.

As in the case of electrolytic diffusion saturation for consistency in producing multicomponent diffusion coatings, it is necessary to periodically correct the composition of the bath for impregnation which changes during thermochemical treatment due to anodic dissolution of the reducing agent and cathodic deposition at the surface of the metal being impregnated.

CHAPTER III

Characteristics of Formation of Multicomponent Diffusion Coatings

The nature of these mediums in which multicomponent impregnation takes place, the mechanism of formation of active atoms and also the basic principles relating to the effect of the composition of the medium on the composition of the diffusion layer, have been discussed in detail in the preceding chapters. Problems related to the formation of multicomponent diffusion layers are discussed in this chapter.

1. INITIAL STAGES OF FORMATION OF A DIFFUSION LAYER

It has been pointed out earlier that the intermediate step in thermochemical treatment, namely, adsorption has not been adequately studied. It is, nevertheless, necessary to deal with this topic, at least in general terms, in connection with the requirements for describing the initial stages of formation of a diffusion layer.

The nature of adsorption processes is exceptionally complex and their qualitative aspects, under strictly identical conditions, strongly depend on the properties and structural state of the metal adsorbent.

During thermochemical treatment, the chemical and phase compositions as well as the structural state of the adsorbent surface do not remain unaltered, in the initial stage of surface impregnation, diffusing atoms are adsorbed at the surface of the metal (alloy) being impregnated, and then at the surface of diffusion layer. These characteristics of the surface, especially during simultaneous diffusion of many elements, have a complex dependence on the technological parameters of the impregnation process. This is the first characteristic that should be considered while evaluating surface phenomena in thermochemical treatments. The second characteristic is that the potential of the diffusion source, as a first approximation (in an extreme case during one cycle of impregnation) can be considered constant, while the same can never be said about the adsorbability of the surface being impregnated. Moreover, at any particular time the adsorptance of different segments of the surface may not be identical. Localization of adsorption at different microportion of the surface, predetermines the preferred locations for nucleation of the new phases of the diffusion layer. Such sites are the most defective parts of the surface.

The nucleation of a diffusion layer appearing in the form of a solid solution can be considered as the simplest case. As an example, we may consider the formation of a stable ferrite in the austenitic matrix of the steel being impregnated. The authors of [135] have experimentally shown that the emergence of the nuclei of a solid solution of silicon in α-iron during siliciding can take place with decreasing probability in the following order: in the adjoining volume of the austenitic matrix at the junction of three austenitic grains, at the interface of two grains, along the lines of dislocations, twin boundaries, and inside the austenitic grain in which the atomic planes of the surface are favorably oriented with respect to the ferrite lattice (satisfying the condition of structural correspondence). The last case is so unlikely that it is never realized except under special conditions (a very coarse-grained matrix, high rate of heating).

During surface impregnation, it is desirable to use the simplest means in order to accelerate and facilitate the process of adsorption. Obviously, the most effective of these would be those which accelerate diffusion. However, for a more precise analysis, it is necessary to separate the two aspects of 'adsorption'. The first is the elementary step involving distribution of the diffusing species at the surface of the metal. This process should be influenced by the same factors which accelerate diffusion. The second is related to a certain stage at which the adsorbed atoms of the potential diffusing species form bonds with a certain group of surface atoms and then begin to diffuse into the volume. This final stage of adsorption is, however, retarded by the three factors which accelerate diffusion (for example, it is accelerated by increasing the number of components in a multicomponent diffusion layer and retarded by increasing the temperature). The rates of these processes depend, in all probability, on a number of factors. The most important among these are the potential of the diffusion source, the nature of the interacting elements, the properties of the phases of the diffusion layer formed, the overall state of the diffusion source, the extent of distortion in the surface, etc.

As indicated above, adsorbed cations can diffuse in the surface and, at a certain stage, into the volume of the alloy being treated. The process of surface diffusion can be distinguished from volume diffusion in many ways. One of these is the so-called 'diffusion relief', i.e. a parallel, stepped unevenness at the surface of the metal crystal, emerging under conditions which also render active surface diffusion possible during thermochemical treatment [136, 137]. Diffusion relief itself is not of practical significance but is proof of the anisotropy of diffusion on a metal surface. Surface diffusion is influenced by the following factors.

The grain size of the metal plays an important role. The diffusion surface is no less dependent on the grain boundary as compared to diffusion in the volume of the metal. For example, the authors of [138] obtained a correlation for surface diffusion, which was earlier known as volume diffusion for quite some time: If the metal is fine grained, the distribution of surface-active impurities depends very little on the orientation of its grains, as diffusion (to be precise, in this case, it should be termed as 'diffusion flow') takes place preferentially along the grain boundaries. In a coarse-grained metal, flow takes place along the grains, in a nonuniform manner and preferably over appropriately oriented grains. In practice, this develops into a so-called 'convective diffusion'; the boundaries of the coarse grains emerging at the surfaces possess such an enhanced power of adsorption that the movement of the diffusion front across the surface takes place, it would appear, in jumps from one grain boundary to another [139]. The frequency of these jumps naturally depends on the orientation of the crystal lattice at the interface. Although with an increase in packing density, the anisotropy of many physical properties of a crystal is evened out [140], the orientation of the structure is bound to significantly influence diffusion on the surface of transition metals: the surface energy of [111] atomic plane in a bcc structure is almost twice the specific energy of the [110] plane. Naturally, this is reflected in the results of surface diffusion [141]. The highest rate of surface diffusion is obtained in planes with highest surface energies [142]. The authors of [143, 144] have evolved the following patterns for surface diffusion.

1. Its rate is in no way less dependent on the strength of the interatomic bond between the diffusing elements and the matrix atom than in volume diffusion; for example, in copper the rate of surface diffusion at the same temperature is lower than that for zinc by a factor of 1 to 2 orders of magnitude.

2. The temperature dependence of the rate of surface diffusion is more than that of volume diffusion. The process may be considered to occur spontaneously above the temperatures threshold. (This temperature threshold, in the case of transition elements, coincides with the temperatures commonly used for diffusion coating).

3. The planes of the fcc structure can be arranged in the following sequence in decreasing order of surface energy (and hence the rate of surface diffusion) [100, 110, 111, 210].

The authors of [145] have investigated the mechanism and role of surface diffusion in systems which, according to the phase diagram, are characterized by total immiscibility of the components (Ag–Ni). Nevertheless, it was found that, here also, surface diffusion proceeds (and quite actively) within a limited thickness of the surface layer of one to two atomic dimensions. In this case the rate of migration of low melting silver is one order of magnitude higher than the rate of diffusion of nickel.

In a number of investigations [146–149 and others] it has been shown that the rate of diffusion at the surface is significantly higher than that in the volume of the metal (alloy). This, apparently, does not need to be discussed further.

At a certain stage in the process of adsorption and surface diffusion, a fraction of the atoms start diffusing in the volume of the substrate metal, forming a solid solution with it. This moment, precisely, should be considered the beginning of formation of the diffusion layer.

It can be asserted with some confidence, that in every thermochemical treatment, the formation of a diffusion layer begins with the formation of a solid solution with the substrate metal as the solvent.

The next state of this solid solution depends on the solubility limit of the diffusing species, on the strength of the diffusion source, the rate of adsorption (v_a) and the rate of diffusion of the element (diffusing species) in the solid solution formed (v_d). With a sufficiently strong diffusion source and a rate of adsorption considerably higher than the rate of diffusion ($v_a \gg v_d$), supersaturation of the solid solution takes place quite rapidly with the formation of a new phase, the rate of growth of which depends on its nature and also on less important factors in thermochemical treatment such as temperature, time, potential of the diffusion source, method of impregnation, etc. Exceptions to the aforesaid mechanism of layer formation are cases of unlimited solubility of diffusing species in the substrate metal, where a phase transformation during impregnation does not occur.

When the rate of adsorption v_a is slower than that of diffusion ($v_a < v_d$) the concentration of the solid solution does not reach the saturation limit and no new phase is formed. Carburizing of steel is a typical example of this type.

According to Arkharov [150] nuclei of the new phase emerge at the surface of the substrate metal by coherent shear (a stage preceding diffusion growth).

The shape and size, which considerably determine their further behavior, depend on a number of structural and concentration factors, such as the correlation between the structures of the matrix and the new phase, development of the surface diffusion process at the interface of these phases, etc.

It can be easily understood that the conditions of adsorption and diffusion change considerably during the formation of a new phase on the surface. This, in turn, significantly changes the rate of the thermochemical treatment itself.

While analyzing the process of formation of the diffusion layer (coating), it is necessary to consider that, during diffusion saturation, diffusion takes place from both sides: By "source" we mean that constituent of the diffusion couple (one of the elements) which possesses, a much higher diffusion mobility than all other components (atomic) in its own medium and, at the same time has a higher chemical affinity toward one of the components of the second constituent of the pair. According to the authors of [151], formation of a diffusion coating involves the following stages:

1. When the interdiffusing elements with considerable difference in their diffusion mobilities are in contact with each other, the fast-diffusing element continues to diffuse in the slow-moving component until a locally varying supersaturated solution is formed around lattice defects in the slow-moving component.

2. Formation of the first nuclei of the new phase at lattice defects with a higher concentration of the diffusing species.

3. Growth of nucleation centers of the new phase in the contact plane (in the case of diffusion saturation, at the surface of the metal).

4. Joining, and a normal (perpendicular to the contact plane of the joint) growth of the first continuous layer of the solid solution.

5. Simultaneous continuation of this growth and the formation of first nucleation centers of the second compound. It is understood that if defects and composition fluctuations were present in the solid solution, they will be intensified in the lattice structure of the solid solution.

6. Transverse growth and joining of the next compound and so on.

Thus, the phase composition of the diffusion coating should be more or less in accordance with the phase diagram, but, with due corrections for the nonequilibrium state of the layer.

It is natural that all the aforementioned processes will affect the overall state of the medium, i.e. the diffusion source. In [152–166] certain aspects of this phenomenon are analyzed. However, in our opinion, it will be premature to draw even qualitative conclusions on the difference (which, of course, exists) between the phenomena of adsorption during gaseous, liquid (metallic bath, fused baths of oxides and salts) and 'solid' processes of diffusion saturation. The experimental data is inadequate for any such conclusion. It is only necessary to note that the catalytic action of the surface under treatment on the process of obtaining active atoms and the process of adsorption are closely related to each other.

While concluding this section, it should be noted that an increase in the number of diffusing elements sharply changes not only the conditions of the adsorption process but also the conditions for formation of the new phases in the layer and the kinetics of their growth.

2. GROWTH OF DIFFUSION LAYER

Interdiffusion and the growth of a diffusion layer are some of the many examples of the tendency of the system to decrease its free energy.

According to the Onsager theory of diffusion [167], the diffusion flux of every component (in a system with any number of components) depends on all the gradients in the system, such as, that of the chemical potentials of all other components, temperature, electric and magnetic fields, concentration of defects, and elastic stresses. Thus, chemical or hetero-diffusion is no more than one of the components of the overall diffusion flux. In general, this component so greatly exceeds the rest that in practice it is only this that is taken into consideration.

Even when analyzing the simplest case of diffusion in a multicomponent system viz. a substitution solid solution of a few 'equivalent' components, it would be natural to assume that this substitution should be accompanied by an increase in the fraction of covalent bonding and a decrease in the diffusion mobility of all the components. The more the retardation of diffusion of other components by a component of the solution the slower they themselves diffuse and, in general, all components retard the diffusion of others [168–169]. In reality, there does not exist such similarity in the electrochemical nature of diffusants nor does a generalized mathematical model of a complex diffusion process caused by the presence of other components.

A general thermodynamic analysis of multicomponent diffusion involves application of the basic laws of diffusion of Fick and Arrhenius [170] to a multicomponent system (in the simplest case—one of three components). This has been exhaustively analyzed by Kondrachenko [171]. Here, not the microscopic aspect (corresponding to the mechanism of the process) but the phenomenological aspect of multicomponent diffusion has been analyzed. It is assumed that, in solids, chemical diffusion is an irreversible process during which the system itself moves toward equilibrium, i.e. toward a concentration homogeneity, on account of its own higher free-energy state, and hence does not require energy from an external source. According to the authors, multicomponent diffusion consists of the following main points:

a) simultaneous impregnation of the metal (substrate) with two (or more) components;

b) simultaneous loss (effusion) of two components from the ternary alloy;

c) subsequent diffusion of two elements in the third;

d) growth of a new phase in the diffusion layer during thermochemical treatment, by interaction between the components.

According to Fick's law, the diffusion of $(n-1)$ elements in the nth metal can be represented as:

$$\frac{\partial C_i}{\partial t} = \sum_{i=1}^{n-1} D_{ij} \frac{\partial^2 C_i}{\partial x^2}.$$

The solution of this equation for an n-component system is a sum of $(n-1)$ terms of which every one, with an accuracy up to the constant coefficient, is the solution of a similar equation for a binary system. In other words, the process of multicomponent diffusion is analyzed as the sum of n one-component diffusion processes.

The biggest hurdle in obtaining solutions to these equations is D_{ij}. The author of [171] has analyzed a three-component metal system where the diffusing species are designated as 1 and 2. Here, the quantity D_{11}, is similar to the normal coefficient of diffusion D, represents diffusion of element 1 under its own concentration gradient and D_{22} has the same meaning for element 2. The quantity D_{21} corresponds to the diffusion of component 2 under the influence of the concentration gradient of element 1.

For complex systems (starting from three-component systems) the problem of phenomenological description of diffusion consists in the fact that for a given surface and initial concentration conditions one cannot unambiguously predict whether effusion of the more mobile component from the alloy takes place or not, i.e. diffusion saturation. This depends on the nature of interaction between elements 1 and 2. In practice the most common case is: $D_{11} \gg D_{22} > D_{12}$ at $D_{21} \to 0$, i.e. when the diffusion mobility of element 1 is significantly higher than that of element 2.

The authors of [172] have termed D_{11} and D_{22} as 'diagonal' and D_{12} and D_{21} as 'cross' coefficients of diffusion. For a three-component system, Fick's second law can be expressed as:

$$\frac{\partial C_1}{\partial t} = D_{11}\frac{\partial^2 C_1}{\partial x^2} + D_{12}\frac{\partial^2 C_2}{\partial x^2},$$

$$\frac{\partial C_2}{\partial t} = D_{21}\frac{\partial^2 C_1}{\partial x^2} + D_{22}\frac{\partial^2 C_2}{\partial x^2}.$$

Generally investigators consider fast-diffusing carbon as element 1 and a transition metal as element 2. Then it can be considered that

$$D_{22}\frac{\partial^2 C_2}{\partial x^2} \gg D_{21}\frac{\partial^2 C_1}{\partial x^2}.$$

Under such conditions, according to the authors of [172], the coefficients of diffusion are of the following magnitudes: $D_{11} = 10^{-9}$ cm^2/s; $D_{12} = \pm 4 \cdot 10^{-10}$ cm^2/s; $D_{22} = 10^{-14}$ cm^2/s; D_{21} = much less as compared to D_{22}.

Separate diagonal and cross coefficients of diffusion were first proposed by the authors of [173] to take into consideration the interaction between impregnating elements during complex diffusion. It was assumed that neither D_{11} depends on the nature of the metal diffusant nor does D_{22} depend on the nature of the nonmetallic diffusant. At the same time the magnitude and sign of D_{12} is determined by the nature of interaction between the impregnating elements themselves. Thus, for example, if element 2 is a strong carbide former, its presence naturally, reduces the thermodynamic activity of carbon (element 1). In such a case, for the purpose of calculation, the value of D_{12} reduces to less than zero. In fact a decisive role is played not by the coefficient of diffusion D_{12} itself, but by the ratio of the two coefficients as expressed below:

$$\frac{D_{12}}{D_{11}} = \frac{E_{12}N_1}{1+E_{11}N_1},$$

where N_1 is the atomic fraction of the element (carbon);

E_{11} and E_{12} are the energies of pair interaction respectively between atoms.

C–C and C the alloying elements.

If the quantity E_{11} is assumed to be negligibly small then it can be considered that the ratio D_{12}/D_{11} is a linear function of N_1 and is independent of temperature and N_2. The calculated data of the effect of carbon and chromium on the ratio D_{12}/D_{11} for different systems is given in Fig. 26 [172, 174].

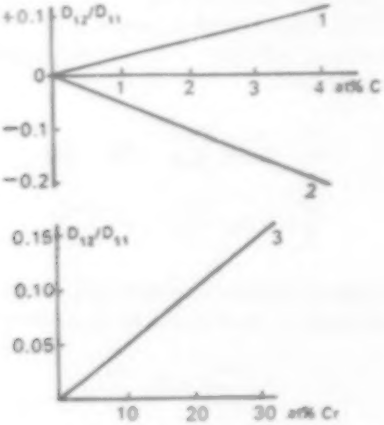

Fig. 26. Effect of composition of austenite on 'cross' coefficient of diffusion: 1—Fe+C+10% Ni alloy; 2—Fe+C+4.8% Cr alloy; 3—Fe+Cr+Si alloy.

The main result of these investigations [171–173] is given as follows. In earlier studies on multicomponent impregnation it was obvious that the distribution of diffusants in the diffusion layer (consequently determining the service properties of this layer), should, as a rule, be smooth. The occurrence of maximums or minimums in the concentration curves was considered an exception [175]. The authors of [171, 172] showed that the existence of an extremum on the concentration curves for diffusion layers is a normal feature, the extreme point being a maximum or a minimum depending on the nature of interaction between elements 1 and 2. In a two-component impregnation the only unknown quantity is D_{12}, as the diffusion coefficients D_{11} and D_{22}, characterize the diffusion in corresponding binary systems and can be calculated before hand [176]. Of course, all these are related to the method of processing of the available experimental data, i.e. for calculation it is necessary to have the concentration curve for multicomponent diffusion layers.

We feel that in the present work it is not necessary to dwell upon the mechanism of diffusion for multicomponent diffusion systems or for processes with diffusion sources of complex composition, as all these aspects are dealt with at length in the monograph [177] by Krishtal.

The growth of a new phase formed during thermochemical treatment deserves more attention.

The most exhaustive theory on the growth of a new phase as a product of solid phase chemical reaction has been explained in the work of Arkharov and colleagues [178–182]. Its main features are as follows: in studies on reaction diffusion, two questions arise—1. How does the atom of the component from the outer medium becomes a part of the solid-phase product of reaction and 2. How is this product transferred, resulting in an increase in thickness of the diffusion layer. The classical approach does not distinguish between reaction diffusion and 'diffusion in general'. It is presumed that the reaction described is a sum of all individual movements of activated atoms. However, not only the fact that the process takes place in a condensed system where the movement of every structural constituent cannot avoid influencing the position of many neighboring atoms, but also that the product of reaction has a complex stoichiometric composition and a unique structure, where every atom should have a definite number of neighbors, located in a specific manner, have not been considered. From this it follows that, as the new phase is in the stage of its inception (at a considerably high rate), activation of atoms in the condensed system must not be of an individual but of a collective nature.

In physical metallurgy, processes such as bainite and martensitic transformations, involving a group movement of atoms, are well known. Asadov and Nasirov [183] have experimentally established that allotropic transformaton of calcium nitrate (at −60°C) takes place 'rhythmically', i.e., according to them, layers of a thickness of 10–20 transform successively in steps to a new modification. Similar results were obtained by the authors of [184] during crystallization of refractory metals from the vapor phase on an inert substrate. The crystals obtained had a layered structure in which the metal in the interior of the layer was chemically pure and the impurities had concentrated in between layers. The authors of this work also observed that the principle of structural and orientational correspondence (the Konobeyevski-Dankov rule) was followed. First an intermediate structure appeared on the substrate which was then followed by a normal equilibrium structure [185].

According to Arkharov, the mechanism of a typical solid-phase chemical reaction can be explained as follows:

1. In the pretransition state, in some parts of the volume a preliminary grouping of atoms of constituent species takes place which distinguishes itself from a supersaturated solution (at a much larger concentration of the impregnating element) as well as from a precipitating phase. The configuration of atoms in such a preliminary grouping is also distinguishable, to a certain extent, from the normal lattices of the original as well as the formed new phase.

2. A small volume, more often with the configuration of a thin disk, the bulk with the structure of the new phase is formed, even without a larger collective shear of atoms (as it is formed basically in the pretransition stage).

3. As the diffusing species continues to be supplied from the external source, the volume of the new phase grows in all directions, including toward the interior—under the edge of the disk. The further they move the greater the lattice is depleted of the metal.

4. This deficiency becomes so high that the internal side of the disk loses coherent relation with the matrix and the disk itself moves in steps in the direction of the excess metal needed by it.

In the theory of Arkharov it is stressed that the proposed mechanism is an alternate route in such cases where diffusion by the normal mechanism is difficult and for every system there is only a particular temperature range within which it can occur. A 'step' or 'jump', according to Arkharov, is preceded as well as followed by normal diffusion along the defects, which is practically impossible below certain temperatures. With an increase in temperature, on the other hand, vacancy mechanism of diffusion becomes possible in the lattice of the new phase also. Therefore, with increasing temperature the length of the 'step' reduces and its frequency increases [181].

A group of atoms, compacted in the pretransition stage with a composition very close to the stoichiometric composition and acting as a cluster, is termed an activated complex [182]. The configuration of the distribution of atoms in an activated complex can be significantly different from the crystal lattice of the product of reaction, but, this structure can be considered equivalent to a part of the lattice with a high concentration of point defects.

CHAPTER IV

Characteristics of Phases in a Multicomponent Diffusion Layer

The selection of impregnating elements for one- and multicomponent diffusion layers is naturally dictated by the desired properties of the coating. If it is necessary to have high mechanical or mechanical plus chemical stability, then a metallic-type compound formation is preferred. In such a case, during simultaneous impregnation with two elements, there is a clear predominance of one of them in the layer; the possibility of the presence of a second element in a metallic phase is determined by its solubility in this phase. It is obvious that in layers formed by metallic phases only the metallic components are, to some extent, 'interchangeable' though, in principle, it has been proved that formation of refractory compounds can take place with the participation of more than one nonmetal.

When it is necessary to combine a chemical and mechanical stability of the diffusion layer with a technological compatability, for example, the ability to undergo plastic deformation, it is considered expedient to use coatings with properties of metallic solid solutions.

Cases of formation of chemical compounds on a metal substrate (by normal diffusion saturation and not by coating in the gaseous or liquid phase) in such a way that both the reactants are also impregnating elements, are apparently very rare (in our experimental results they are nonexistent).

Any diffusion layer (except when there is an unlimited solubility of the diffusants in the metal being impregnated) is multiphase (the number of phases being not less than two). Characteristics of the basic phases in multicomponent diffusion layers are, briefly, given below.

1. MULTICOMPONENT SOLID SOLUTIONS ON A BASE OF SUBSTRATE METAL

It cannot be claimed that surface alloying of metals by several elements with the formation of a solid solution-type coating was not studied earlier. The reason for the limited data on this subject [187, 188 and others] is that attention was mainly paid to the study of properties, rather than the structure of the layer obtained. Thus, analysis of the parameters leading to a certain type of structure and consequently its properties is, in general, completely lacking.

It does not provide a basis for even a qualitative prediction of the effect of conditions of surface impregnation on properties of the layer and ways and means to improve these.

It is precisely for this reason that it is necessary to analyze the nature of solid solutions in multicomponent layers and to study the correlation between the structure and properties of solid solutions.

It is well known that even liquid solutions, except those practically nonexistent 'infinitely dilute' solutions, cannot be considered to be singular systems (i.e. exhibiting a linear relationship between the physicomechanical properties and concentration, which is possible only in the total absence of a chemical interaction between the components). Solid solutions should be classified as nonsingular or an irrational systems [189–191]. It is precisely due to this that even very small concentrations of solute elements (especially metalloids) so sharply influence the physical properties of solutions—substitutional [192] as well as interstitial [193]. In other words, 'infinitely dilute' or 'singular' solid solution is perhaps only of an abstract value—which can be hardly used to describe solid solutions in diffusion layers.

During the formation of a solid solution, atoms of solute components are distributed preferentially at structural defects of the solvent, not only along grain boundaries, but all over its volume. Distribution of the dissolved components in solid solution can be qualified in terms of energy levels [194]: the highest energy site of the atom is the lattice-site (in the case of substitution) or at the regular interstitial (in the case of interstitial solution) in an 'ideal' lattice structure; much lower energy site of the solute atom occurs near a vacancy (a vacancy-atom complex); along the axis of a dislocation; along the boundary grain (small-angle grain boundary); along the large-angle grain boundary; and at the surface of the metal.

From the foregoing it follows that a correlation must exist between the structure and state of the solid solution and the diffusion mobility of its components.

It is known [195] that the lattice constant of a solid solution is directly proportional to its composition, and the effect of solute concentration on the rate of diffusion is very complex. Generally, when diffusion saturation is intended to obtain coating properties considerably distinct from the properties of the metal being impregnated, diffusing species which sharply differ from the base metal in respect of their electronic structure, are used. In such a case, the rate of diffusion in solid solution, as a rule, decreases sharply as the solute concentration increases [196, 197]. At sufficiently low temperatures, the diffusivities of the components of the solid solution sharply fall owing to atomic interaction. This also takes place in case of an unlimited intersolubility [198].

However, a very strong interaction of the components is observed in interstitial solid solutions. From simple 'pure geometric' considerations it follows that the presence of interstitial impurities should retard the diffusion substitution on a nearby site [199] and vice versa [200, 201].

The role of the geometric factor-correlation between the atomic dimensions of the components and the structure of their lattices is well known for two-component substitutional, as well as, interstitial solutions [202, 203]. This factor plays a still more important role during the formation of multicomponent solutions. For example, substitution of a fraction of the 'large atom size' component of the solution by the 'small atom size' component can lead to an abrupt expansion of the range of phase homogeneity, and even to an unlimited solubility in the ternary system (with a limited solubility in the binary system).

Still, a much of the behavior of components in a multicomponent solid solutions is not very clear. It has been established, for example, that the interaction between electrons and their redistribution during a temperature variation can even change the sign of the charge on the ions of the dissolved element [204].

However, the maximum influence on the behavior of the components of a multicomponent solid solution—significantly much stronger than in the case of two-component systems—is due to the concentration factor.

Glazol et al. [205] and the Kidius group [206] have established that in three-component substitutional solid solutions (Cu–Ni–P, Fe–Al–Si), in the temperature and concentration ranges in which, according to their phase diagrams, no indications of any structural changes, sharp variations in physical properties are observed (microhardness, microthermoelectromotive force). This points to the state of approaching readiness of such solid solutions for ordering, in which even favorable conditions have not yet set in.

Generally, speaking the ordering phenomenon of a binary system without taking into consideration the driving force for ordering, the tendency of atoms of components of a solution to get distributed in space, as farther as possible from each other, must increase with an increase in the number of components in the system. If, for example, we consider a solution of two 'unequal' components *A* and *B* in a metal *C* even in such a system of minimum components, there are three possible variations:

1. Disordered solutions: *A*–*B*–*C*.
2. An ordered distribution of atoms *C* with a random distribution of *A* and *B* at definite lattice sites of *C* but without any sign of ordering. (A wide range of ratios of components A/B is possible at an almost constant ratio $A+B/C$.)
3. An ordered distribution of atoms of all three types at a certain (depending on the geometry of the structures) definite ratio of concentrations $A/B/C$ [207].

An important quantitative difference between multicomponent and binary solid solutions is that the actual variation in properties, which is due to ordering, is observed not only in narrow concentration intervals, but over a very wide range due to the prevalent phenomenon of short-range order. On introduction of a third component in an existing binary solid solution, the spatial energy distribution of bonding electrons becomes complicated. In order to maintain the stability of the crystal structure, the third component should interact with the second component in such a way that the average charge of the atom in solution remains unchanged. The simplest is ordering with a short-range order [208]. The ordering mechanism may vary depending on the temperature: at low temperatures there is a diffusionless variation and at high temperatures there is an antiphase ordering mechanism.

If the binary system has a superlattice structure, its preservation in the three-component system depends on the nature of additional diffusing species. If the nature of the components of the binary superlattice structure is similar, and the new component does not induce any variation in the electronic structure, it is possible to preserve the superlattice structure over a wide concentration range of a ternary system (e.g., the Cu–Au system on addition of Ag to it). If the quantitative ratio of the components of a binary superlattice structure is very different from 1 : 1, and if their natures are also widely different (e.g., iron–silicon and iron–aluminum superlattice structures), introduction of a third component to the system, especially if it replaces that component of the ordered solution whose concentration is lower, will first lead to a rapid breakdown of the long-range order and then to a breakdown of even a short-range ordered distribution of the atoms of the former superlattice structure. In case it is necessary to create a superlattice in the layer, it is apparently expedient to carry out complex diffusion saturation with silicon and aluminum alone.

The main effect of the ordering phenomenon in a multicomponent diffusion layer is that it quite sharply retards the diffusion processes.

It should be understood that the phenomenon of short-range ordering which is highly probable in complex solid solutions, as analyzed above, cannot be revealed by metallographic techniques and can be detected only by fine measurement of some of the physical properties, even though its influence on the rate of diffusion may be very significant. The even more significant effect on the type of bonding and processes taking place in the solution should be revealed by the formation of an interstitial solution. The existence of a wide range of homogeneity in such a solution is a rarity. Apparently, only hydrogen has a high solubility in transition elements [210]. However, here also the predominance of the electrochemical over the geometric factor can be well detected from geometric considerations: a considerable solubility of hydrogen should be exhibited in practically all the transition elements, whereas in reality its solubility is closely related to the electronic structure of the metal, for example, it induces in the direction from titanium to nickel. Undoubtedly, hydrogen in interstitial solution interacts with the solute metal, as indicated by the recently discovered ordering in solid solution of hydrogen in the superlattice of Cu_3Au [211].

If, in substitutional solutions, statistically the disordered state of different types of atoms is at best a first approximation than the actual structure, then for interstitial solutions, not satisfying Hegg's relation, ordering must be a normal case and not an exception. It is difficult to contest this view expressed by Belotsky et al. [212, 213]. The phenomenon of ordering in interstitial solid solutions was first observed in dilute (up to 1 wt.%) solutions of oxygen in niobium and tantalum [214]. One of the reasons for ordering in this case is that in interatomic bond formation oxygen is the donor atom. Based on studies of physical properties of solutions, it has been established by Volkov [215] that the tendency to ordering in the case of interstitial is a common feature of many systems including Fe–C, Fe–N.

As in the case of substitutional solutions, ordering in the case of interstitial solid solutions (if it occurs) should lead to a decrease in diffusion mobility of components of the solution in the volume.

2. INTERMETALLIC COMPOUNDS

During diffusion impregnation of transition metals, (including multicomponent impregnation) intermetallic compounds may be formed in the diffusion layer. Transition metals first form such compounds with nonmetals such as B, C, N, P and others. The crystal chemistry and electronic structure of phases of this class have been fairly well studied and described in detail in the works of Samsonov et al. We shall consider only those aspects which are directly related to diffusion saturation.

Intermetallic phases can provide diffusion coatings with better service properties. However, this presumes a high strength of the interatomic bond and consequently, a low diffusion mobility of the components of the compound. Therefore, the rate of growth of many diffusion layers containing such phases is very low [216]. In many coatings of these phases, it is not possible to identify the grain boundary between adjoining crystals (for example, in carbides and nitrides). This, and also the slow rate of growth of these layers confirm the limited role of intergranular diffusion. Apparently, in such cases, diffusion directly through the crystal lattice of the intermetallic phase is predominant.

The modern theory of interatomic bonding in intermetallic phases is based on the fact that the spatial energy distribution of the bonding electrons in the phase structure is determined by the statistical weight of atoms with a stable electron configuration (SWASC) of components in a free state. It supports the view that there is little difference between the physicochemical properties of different compounds of the same metal and nonmetal [217]. Silicides of titanium can be cited as an example [218].

Only a minimum variation in the properties of the phases is observed when the metallic component of the intermetallic compound is substituted by another metal belonging to the same subgroup of the periodic table retaining the same nonmetallic component. For example, there is a very close 'kinship' between the monocarbides of titanium, zirconium and hafnium [219]. A changeover to another class of compound of the same metal, i.e. substitution of the nonmetallic component leads to a sharp change in the whole set of properties. However, compounds of all the different classes (borides, carbides, nitrides and others) have as many similar features, as different ones, in their crystal chemistry and consequently in their diffusion behavior. The diffusion mobility and rate of growth of diffusion layers (phases in the layers) are directly related to the following factors:

a) Imperfections in the structure, the composition and the possibility of ordering of defects in them;

b) The mechanism of diffusion movement of metallic and nonmetallic atoms in the structure;

c) The possibility of a substitutional solution of metals and nonmetals in the structure of the substrate and formation of multicomponent phases (with more than two components).

It is known that monocarbides of transition elements (mainly titanium and vanadium) correspond to the composition MeC_{1-x} where $x>0$. The range of homogeneity for such compounds is directly related to the electron configuration of the components. From the theory proposed by Samsonov et al. [220], it follows that the range of homogeneity of carbide phases must reduce with transition from titanium to chromium. In phases of type $Me_x^{VI}C_y$, it is practically absent, and the carbides acquire a complexity of structure and stoichiometry. This also applies to other metallic phases such as nitrides albeit to a lesser extent.

It is necessary to appreciate the practical importance of carbides during diffusion saturation.

It is believed that the existence of structural imperfections in monocarbides of metals of groups IV and V (and also other metal-like phases) is their inherent property, i.e. at $x=0$ phases MeC_{1-x} cannot generally exist [221–223]. This view does not seem to be correct. The monocarbides of titanium [224] and vanadium [225] obtained, at present, in the structure for which the condition $x=0$ holds good. The deficiency in the structure of these phases with respect to carbon arises on account of the existence of a nonequilibrium condition during their formation, i.e. the condition under which they form does not ensure a complete homogenization which is essential for avoiding these defects.

Increase in structural imperfections (x) increases the mobility of components, and diffusion permeability of phases [226–230]. It points to certain basic features of the diffusion mechanism in intermetallic phases: diffusion takes place along sublattices, i.e. for diffusion, the metal and nonmetal atoms use vacant lattice sites in their respective sublattices.

It has been established [231] that in carbide, nitride and hydride of zirconium, more or less detectable diffusion mobility is observed only at $x>0$, while nonmetal diffuses along vacancies in its own sublattice and the diffusion mobility of the metal is close to zero. In the carbide, $Me_{23}C_6$, the structural defects are not high and the concentrations of vacancies in the metallic and carbon sublattices are approximately the same; every component diffuses along its own sublattice [232]. At $x=0$, in the monocarbide of vanadium, vacancies develop in the metallic sublattice and so also the corresponding possibility of diffusion of metal atoms which was otherwise not observed in the structure with defects with respect to carbon [224]. A qualitatively similar case is that of silicides of transition metals: silicon is the only element with any appreciable mobility [233].

This is still more pronounced in compounds, distinguished by their high strength due to very close resemblance of the components which are neighbors in the periodic table: For example, in silicon carbide, due to the absence of vacancies, diffusion of neither carbon nor silicon is observed [234].

As a rule, borides of transition elements do not have a region of homogeneity. Diffusion of boron in them occurs through the defects of its sublattice [54]. It has not been established whether boron can also diffuse along the vacancies, which are certainly present, in the metallic sublattice as in the case of carbides [235]. It should be noted that boride and silicide coatings of significant thickness are often obtained within a short period. As this is difficult to explain on the basis of structural defects alone, it should be remembered that the layers of these phases have well developed grain boundaries. Probably grain-boundary diffusion plays a very significant role in the formation of these coatings.

The fact that a preferred diffusion through their 'own' sublattice occurs has also been established for nitrogen in nitrides [236], oxygen in refractory oxides [237, 238] and hydrogen in hydrides [239, 240]. From this analysis it follows that diffusion in sublattice is due to the high strength of the interatomic bonding in a number of compounds and the occurrence of diffusion by such a mechanism in more or less 'pure form' leads to a very low diffusion permeability of the phases and a small thickness of the diffusion layers.

For increasing the intensity of diffusion saturation it is necessary to create conditions of equivalence of 'diffusion' for both the components of the phase, for example, by increasing the impregnation temperature or by alloying of the layer [241–244]. It is also necessary to study the properties of the metal forming the phase, for example, with an identical diffusion mechanism in intermetallic phases the rate of diffusion in phases formed by titanium is lower than that in compounds of chromium or molybdenum [245].

In recent years a lot of fresh data has been collected on the properties of intermetallic compounds. Authors of [246] have established that in phases of the AB_{1-x} type where A is niobium or titanium and B is carbon or nitrogen, the emergence of an ordering of vacancies in the carbon sublattice is observed at sufficiently high values of x. Such a phenomenon is a direct indication of the possibility of existence of a ternary carbide phase. These are also applicable to diffusion layers. The intersolubility of metal carbides has long been known [247]. However, only recently incipient short-range ordering has been observed in a number of pseudobinary carbide systems, exhibiting a wide range of intersolubility: VC–WC, NbC–TiC, NbC–WC and others [248].

The data provided by Samsonov et al. [249] is most interesting. It has been established that hydrogen ions can be distributed in an ordered manner in structural defects in monocarbides of titanium and zirconium. In addition to 'carbohydrides', 'hydronitrides' have also been found. The question of interchangeability of other nonmetals in refractory compounds still remains open as the evidence available to data is contradictory [250–252].

There appears to be considerable agreement amongst various investigators on borides. Borides of iron are practically free of other nonmetals, in spite of the higher amount of structural defects in the diffusion layer. Similarly, it has been established that carbon is almost insoluble in borides of niobium, tantalum, molybdenum and tungsten [253]. In the literature, a fairly large number of cases of ternary compounds of one transition element with two nonmetals are reported. We shall not analyze this data as, it is not sufficiently reliable. There are no two studies on ternary compounds of an identical system the results of which agree with each other. The properties of these 'ternary' compounds are very similar to those of phases based on binary systems. While analyzing complex diffusion coatings, it is necessary to take into consideration that the 'interchangeability' of metals in metalloid phases is possible provided the electron configurations of the metals similar to each other and the possibility of substitution of one nonmetal by another in the intermetallic phase is relatively limited or zero. The probability of formation of a diffusion layer of a ternary compound with its own typical crystal structure is not completely ruled out. However, it is most likely that one cannot be produced under normal conditions of diffusion saturation.

3. INTERMETALLIC PHASES

In multicomponent diffusion saturation, generally, one of the components is a covalent nonmetal and the second is a transition metal. Under such conditions a metallic diffusing species never forms any compound with the substrate metal as the nonmetal-metal chemical affinity is always significantly higher. However, in many cases, nontransition metals (aluminum, zinc and others) are used for diffusion saturation and there arises a possibility of formation of their compounds which differ from metalloid compounds in their properties.

According to current understanding [254], the main factor determining the possibility of the emergence of sufficiently strong compounds from an interaction between transition metals is the redistribution of *d*-electrons in order to maximise the statistical weightage of atoms with the stable electron configuration of both the components. Therefore, the formation of comparatively strong compounds is possible among metals with $N_d \leqslant 5$ and metals with the number of electrons in their *d*-orbitals ranging between 6 to 10. For this reason only, the majority of these are strong carbide formers and, therefore, during surface impregnation of steels they neither interact with iron nor among themselves, but with carbon present in the steels [255]. Exceptions to this are Laves phases, which can form even between components with very similar electron configurations. However, in systems of transition metals these are not very common.

For diffusion saturation, it is necessary that these compounds should not deviate from high strength [256]. Therefore, the service properties of the layer provides not so much the stability of the intermetallic compounds itself as the concentration of the diffusing species and the nature of its interaction with the environment from which the substrate metal is to be protected. For example, on aluminizing steel, the diffusion coating protects it from high-temperature corrosion irrespective of whether aluminides exist in the diffusion layer or not [257]. Aluminides with maximum strength are formed with titanium and vanadium and also with nickel; metals occurring in between them, however, do not produce stable aluminide phases [258]. Consequently, during diffusion impregnation of metals and alloys with metals the formation of intermetallic compounds in the coating is possible only if the other diffusants are not capable of forming more stable compounds (for example, intermetallic compounds).

As in the case of metalloid phases, intermetallic compounds can also serve as bases for the formation of complex (multicomponent) solid solutions.

In some cases even an unlimited intersolubility of intermetallic compounds is observed. Thus, in [259] an extremely rare case of complete intersolubility between compounds with hexagonal structure: Ni_3Ti–Ni_3Nb–Ni_3Ta, and with body-centered cubic structure: TiFe-TiCo-TiNi, have been reported.

It has been established that in ternary (more complex) systems the redistribution of electrons during interatomic bonding can be so complex that prediction of the properties of the product from a knowledge of the characteristics of the basic components, which is possible to some extent for binary systems, is impossible. Kurnakov's law of variation in properties with change in composition is, also, not applicable to ternary systems. Here neither a gradual change in properties nor their additiveness is observed. On the basis of available information [260–262] on diffusion processes in compounds the following generalization can be made. Three types of diffusion can occur in compounds with the following characteristics:

1. The components of the compound are very similar to each other with respect to their electrochemical nature and the size of their atoms (The Hume-Rothery phases and those similar to them); the type of interatomic bonding is predominantly metallic; there is a possible 'interchangeability' of the component atoms in the lattice and diffusion through any sublattice and the diffusion mobility of the components is sufficiently high so that deficient solid solutions are not formed.

2. The components of the compounds are also similar, but with a preferred covalent bonding, i.e. these are either semimetals or nonmetals (compounds of arsenide of gallium, magnesites, beryllides, carbides of boron and silicon and others). The possibility of a slight deviation from the stoichiometric composition on either side with the formation of the deficient solid solution and diffusion is determined by the strength of the bonding: in semimetallic phases diffusion is fairly intensive while in nonmetallic phases it is restricted; in any case the diffusion mobility is many times lower than that in phases of type 1.

3. Components of compounds with different properties (metal-like phases). Deviation from the stoichiometric composition—often quite significant—is mostly due to a deficiency of metal atoms; the rate of diffusion of the latter (almost exclusively through its 'own' sublattice) can be quite high. The rate of diffusion of metal (only along a metallic sublattice) is very low, up to temperatures close to the melting point; and there is a vacancy mechanism of diffusion.

4. INTERACTION BETWEEN PHASES IN MULTICOMPONENT DIFFUSION LAYERS

In multicomponent diffusion impregnation, cases in which the diffusion layer consists of only one phase are rare. Moreover, if by the 'layer' is understood the entire fairly deep zone, which due to an inflow of diffusants from the surface is distinguishable from the original metal, if not with respect to phases but with respect to chemical composition, then it appears that one-phase layers are uncommon. It is, therefore, necessary to consider how these phases interact during the growth of the layer, undergo transformations, and the manner in which this is reflected in the final structure.

The basic principles of the theory of topochemical (solid state) reactions, which are equally applicable to diffusion saturation are given in [263]. They are:

1. *Principle of continuity*. Chemical compounds (phases) formed during any topochemical reaction, cannot interact with the original solid materials under the (same) given conditions, i.e. the equilibrium of the reaction between the diffusion-source material and the layer material moves strongly in the forward direction.

2. *Principle of succession.* In a complex chemical process, successively formed compounds (phases) must have increasing thermal and thermodynamic stabilities and should correspond to an increasing level of transformation.

Thus, according to this principle, the formation of all phases existing in the phase diagram of the corresponding system with increasing concentration of the impregnating element cannot be avoided.

3. *Principle of independence.* Every reaction which is distinguished by its mechanism can occur irrespective of the occurrence or nonoccurrence of other reactions.

One of the main points of dispute in the theory of structure formation in diffusion layers is whether specific features of the diffusion mechanism influence the phase composition of the layer, i.e. whether the difference between the degree of equilibrium in the diffusion layer and the phase diagram is reflected in the quantity and distribution of phases in the layer, or not. Normal metallographic study of a large number of costings has revealed the absence of phases in them which were otherwise indicated by the phase diagrams. This phenomenon is clearly observable in multicomponent impregnation.

Guzev et al. [264] consider that this is a normal phenomenon and observe that the absence of any phase in the diffusion layer, in spite of its presence in the phase diagram, can be due to either a very low coefficient of diffusion in this phase or a very small concentration zone of its occurrence in the phase diagram.

Thus, it is established that the cause of incompleteness of phases in the diffusion layer is the same diffusion selection which leads to morphological and crystallographic textures. However, on more precise analysis it appears that the diffusional choice, if it exists, should lead to opposite results. A phase with a narrow range of composition, in order to avoid a breach of the principle of continuity of diffusion flux, should exhibit not a low, but a significantly high diffusion permeability [265].

Further, if it is considered that the main diffusion flux in a multiphase layer passes through, first of all, not by the crystallites of phases in the layer, but by the defects of the boundary volumes (i.e. diffusion does not depend so much on the lattice structure in its 'ideal' defects-free state, as much on the extent of imperfections and the effect on it of factors such as temperature). It can then be asserted that at a sufficiently high potential of the diffusion source and under sufficiently favorable conditions diffusion in the layer will be an aggregate of all the phases, existing in equilibrium phase diagram. Thickness of individual (layers) is also determined not by the absolute value of the coefficient of diffusion in them but by the correlation of diffusion rates in all (or at least the adjoining) phases of the diffusion layer. A few examples are given here to support these statements. In [266], during diffusion saturation of molybdenum with silicon, Arzamasov has obtained a coating which consisted of successive layers of all the silicides of molybdenum. In this case it is also significant that the thickness of molybdenum–silicide layers decreased with decreasing silicon content ($MoSi_2$—80, Mo_5Si_3—18 and Mo_3Si—2–3μ; this does not tally with the width of the zone of homogeneity for silicides (only Mo_5Si_3 has a significant zone of homogeneity). Similar results were obtained for aluminizing of molybdenum [267], siliconizing of titanium [268] and others, and also in our investigations on siliconizing and aluminizing of tungsten and molybdenum by different methods. One of the main consequences of the nonequilibrium structure of diffusion layers is their discontinuity, in other words, diffusion porosity. The mechanism of formation of diffusion porosity has been fairly widely studied and discussed in detail in our monograph [121]. Therefore, the results of only a few qualitative observations on this phenomenon in multicomponent diffusion layers are discussed here. Initially, it may appear that the increase in the number of elements being simultaneously impregnated should considerably increase the danger of formation of a porosity. However, in practice, the tendency toward the formation of a porosity does not increase during multicomponent diffusion saturation. Moreover, in multicomponent impregnation, pores do not form even in those phases in which pore formation is considered unavoidable during one-component surface impregnation. There can be many reasons for this. Firstly, in solid solution type layers (including those based on chemical compounds), an increase in the number of components, as a rule, leads to a decrease in the diffusion mobility of each of them (especially for the transition metals at the temperature normally used during thermochemical treatment) and therefore, the ratio between the rates of diffusion changes in favor of the least mobile (substrate) metals.

Secondly, in general, the thickness of multicomponent layers is less than that of most rapidly diffusing element of the complex diffusion source, and porosity begins only at some depth below the interface of the phase prone to pore formation. Further, during multicomponent diffusion saturation the normal number of phases in the diffusion layer is generally not larger than in the 'basic' one-component layer, and, therefore, the probability of an increase in porosity does not increase.

PART TWO

Two- and Three-component Coatings on Iron and Steel

CHAPTER I

Two-component Diffusion Coatings Containing Aluminum

1. BOROALUMINIZING

Simultaneous diffusion coating of metals and alloys with boron and aluminum (boroaluminizing) is carried out to improve both the wear and heat resistance and, sometimes, for improving corrosion resistance in different corrosive mediums.

To date three methods of boroaluminizing have been tried out in laboratories: boroaluminizing in powders of materials containing boron and aluminum [24, 65, 269–271], in melts of Na_2O–Al_2O_3–B_2O_3 and Al_2O_3–B_2O_3 systems, by electrolysis [80, 82, 128, 272] and by using a gaseous phase [273].

Diffusion saturation of iron and plain carbon steel simultaneously with boron and aluminum in powder systems consisting of boron carbide, ferroaluminum (50% Al) and activators such as borax and ammonium chloride has been described in [24, 65, 269–271]. Ferroaluminum can be replaced by a mixture of aluminum powder and alumina in the ratio of 1 : 5.

Surface alloying is carried out in the temperature range of 800° to 1050°C in containers provided with fusible shutters.

Processing for 6 h at 1050°C is recommended as an optimum treatment for boroaluminizing. The results of diffusion coating—thickness, structure and constituent phases of the layer—are strongly influenced by the composition of the active mixture (Tables 5 and 6).

Table 5

Composition of mixture, %		Constituent phases of boroaluminized coating (1100°C, 6 h)
84% B_4C + 16% $Na_2B_4O_7$	97% FeAl + 3% NH_4Cl	
90	10	FeB, Fe_2B, Fe_3Al
80	20	Fe_2B, Fe_3Al, FeAl
70	30	Fe_2B, FeAl
50	50	FeAl, Fe_2B

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Table 6

Composition of the mixture, %		Thickness of the boroaluminized layer, μm (1050°C, 4 h)		
84% B_4C + 16% $Na_2B_4O_7$	97 FeAl + 3NH_4Cl	Commercial iron	Steel 45	Steel U8A
100	0	397	362	325
90	10	386	356	327
80	20	361	335	305
70	30	318	287	262
60	40	286	259	221
50	50	245	227	199
40	60	247	218	202
25	75	290	273	244
0	100	375	340	318

When boroaluminizing is carried out in mixtures containing up to 15% of FeAl, the diffusion layer has a typical acicular structure and consists of borides FeB and Fe_2B. An increase in the ferroaluminum content from 15% to 50% leads to the disappearance of FeB and the formation of a solid solution of aluminum and boron in α-iron. The boroaluminized layer obtained by surface impregnation in a mixture containing 50% FeAl, consists mainly of solid solutions of aluminum and boron in iron (surface zone) and insignificant quantities of borides contiguous to the base metal. On further increasing the FeAl content in the mixture, the thickness of the outer zone of the layer increases and that of the inner zone (borided) decreases.

The microhardness of the outer zone reduces along the depth of the diffusion layer, i.e. from the surface to the center of the workpiece and ranges from 450 to 330 kg/mm². Boride phases have a high microhardness (up to 2200–2600 kg/mm²).

The thickness of the diffusion layer varies with the ferroaluminum content of the impregnating mixture and is minimum at an FeAl content in the mixture of about 50% or a pure aluminum content of 10–15%. The plot of thickness of the diffusion layer versus the composition of the melt is given in Fig. 27 (See Fig. 5 a, b).

The presence of minimum indicated above can be explained as follows:

Aluminum has a very limited solubility in borides of iron, whereas, boron is almost insoluble in aluminide phases (including α-solution). Therefore, addition of either of these elements in the charge (impregnation mixture) for multicomponent impregnation should first result in a reduction in the coating thickness, leading finally to a discontinuity in the composition of the layer. This is followed by the formation of phases based on the second element. For

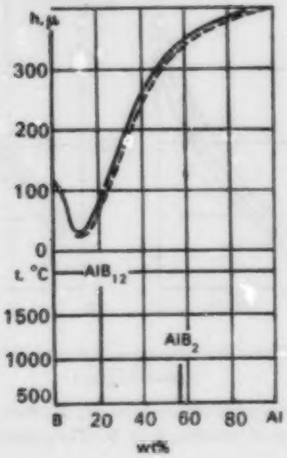

Fig. 27. Variation in thickness of diffusion coating with composition of mixture for boroaluminizing in a mixture of pure powders of diffusing species.

example, addition of aluminum to boron-containing materials first reduces the thickness of the borided layer, as aluminum practically unable to penetrate through the borided layer and, in such a case, acts as an inert addition. With a further increase in the aluminum content of the mixture the potential of the diffusion source falls to such a low level that the boride coating formed at the surface is not continuous. In the spaces between boride phases particles of aluminides are formed. Gradually the number of these prevail and the thickness of the layer increases owing to the increase in the potential of the diffusion source of aluminum.

An increase in temperature, increases the thickness of the layer (Fig. 28) and leads to a widening of the zone of simultaneous impregnation due to a narrowing of the zone of pure boriding. In such cases the zone of pure aluminizing also increases slightly. From the technological point of view, the boroaluminizing process in pulverized mixtures is a comparatively simple method and does not create any problem in its conduct. However, boroaluminizing mixtures, based on boron carbide or amorphous boron and ferroaluminum (aluminum powder) described in [24, 270, 271] are very expensive. From this point of view, boroaluminizing using powder oxides (aluminothermic process)* is a much more promising method. In this case boric anhydride acts as the source of active boron atoms.

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*Developed by M.H. Martinyuk, G.M. Levchenko and G.V. Borisenko with the guidance of the authors [105].

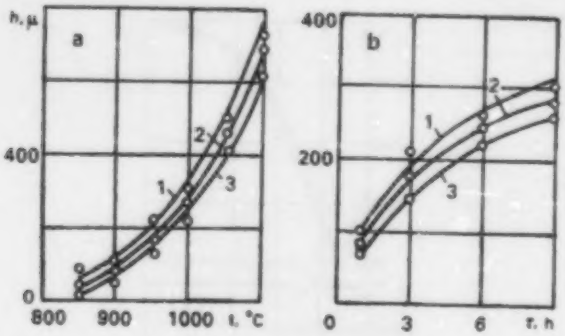

Fig. 28. Kinetics of boroaluminizing in mixtures of boron carbide and ferroaluminum:

1—Armco iron; 2—Steel 45; 3—Steel U8:
a—Duration of process, 6 h; b—Temperature 1000°C.

The effect of the ratio of boric anhydride and aluminum, at constant concentrations of aluminum oxide and sodium fluoride, on the formation of a boroaluminized layer is shown in Fig. 5 (c). A complex boroaluminized coating is formed at concentrations of aluminum in the mixture ranging between 35–40% and 60%. At lower concentrations of aluminum a preferred boriding takes place, whereas at higher levels aluminizing occurs. At 50% of Al, a minimum is observed on the curve. The reason for its occurrence have already been discussed.

The composition of impregnating mixtures for boroaluminizing was optimized on the basis of the results of metallographic analysis (Table 7) and investigations on thermal stability and wear resistance of boroaluminized steels.

If a higher wear resistance is required a mixture of the following composition is recommended: 99.5% [70% Al_2O_3 + 30% (60–50% B_2O_3 + 40–50% Al)] + 0.5 NaF. The mixture—99.5% [70% Al_2O_3 + 30% (40–45% B_2O_3 + 60–55% Al)] + 0.5% NaF can be used for obtaining a surface layer with a high thermal stability.

The effect of the duration of processing on the thickness of a boroaluminized layer during impregnation in a mixture of optimum composition is shown in Fig. 29.

It can be seen, from the given data, that as far as the kinetics of diffusion-layer formation are concerned, these mixture compositions are no way inferior to those known earlier.

On boroaluminizing under optimum conditions, the diffusion layer on iron and carbon steels has an identical microstructural composition, irrespective

Table 7

	Mixture composition, wt. %				Impregnation parameters		Thickness of boroaluminized layer, μm			
	[A% Al_2O_3 + (100 − A) % (x% Al + y% B_2O_3)] + n % NaF						Material			
No.	Al_2O_3	Al	B_2O_3	NaF	t, °C	τ, h	Commercial iron	Steel 20	Steel 45	Steel U8
1	70	50	50	0.5	900	2	65	55	40	35
2	70	50	50	0.5	900	4	105	80	55	30
3	70	50	50	0.5	900	8	140	125	105	90
4	70	50	50	0.5	950	2	140	105	95	75
5	70	50	50	0.5	950	4	175	140	140	125
6	70	50	50	0.5	950	8	210	210	160	140
7	70	50	50	0.5	1000	2	245	210	180	165
8	70	50	50	0.5	1000	4	280	245	210	180
9	70	50	50	0.5	1000	8	315	280	245	215
10	70	60	40	0.5	1000	2	180	160	140	105
11	70	60	40	0.5	1000	4	280	260	230	200
12	70	60	40	0.5	1000	8	350	320	280	260

of whether the ratio of $B_2O_3 : Al$ in the impregnating mixture is 50 : 50% or 40 : 60%. The sequence of its occurrence from the surface to the volume is as follows:

$$Fe_2Al_5 + FeAl + Fe_3Al + \alpha\text{-phase} + Fe_2B.$$

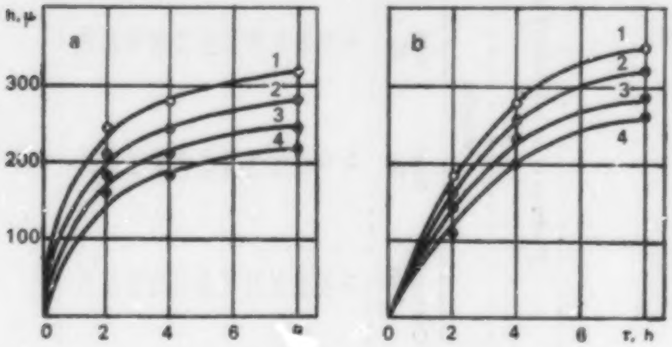

Fig 29. Kinetics of aluminothermic boroaluminizing of (1) Armco steel; (2) Steel 20; (3) Steel 45; (4) Steel U8 at 1000 °C:

a—Mixture composition: 70% Al_2O_3 + 30% (50% Al + 50% boric anhydride) + 0.5% sodium fluoride mixture; b—Composition: 70% Al_2O_3 + 30% (60% Al + 40% B_2O_3) + 0.5% sodium fluoride.

These are distinguished in respect of the extent of the zones of aluminide and boride phases. In the first case the boride phase is predominant, while in the second aluminides are more prominent (Fig. 30).

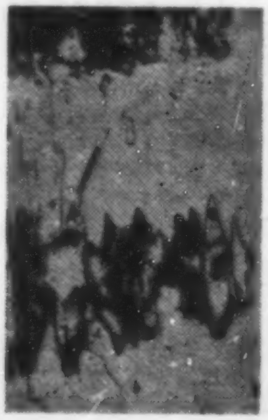

Fig. 30. Structure of boroaluminized coating (× 200) on diffusion saturation with a predominant mixture of aluminum.

The microhardnesses of Fe_3Al_5 and Fe_2B lie in the ranges 790–675 and 1680–1620 kg/mm², respectively. The boride phase adjoins the central core. The microhardness of the solid solution varies between 430 to 280 kg/mm².

The concentration of aluminum, on the surface of steel 45, after boroaluminizing in a mixture with $B_2O_3 : Al = 40 : 60$ wt.% is found to be 41.0%.

To some extent boroaluminizing using a paste containing amorphous boron and aluminum powder, (2 to 10%) can be considered as one of the variations of boroaluminizing by the powder method [274].

An aqueous solution of silicate gum (2%) was used as a binder.

The samples were polished and degreased before boroaluminizing. Specimens with 2 mm thick paste coating were first dried in air and then in a drier at $t = 100$°C for 1.5–2 h. Subsequently, they were placed in a container at a distance of 5 to 10 mm from each other and were covered with an inert material—alumina or chamotte. Before starting the process, the container was sealed. Surface impregnation of carbon steel was carried out for 1–6 h in the temperature range of 950–1050°C, whereas steel Kh18N9T (18–9 stainless steel) was boroaluminized at a much higher temperature range—1100–1200°C.

The thickness of the diffusion layer is considerably influenced by the composition of the paste (Fig. 31). The thickness of the diffusion coating on carbon steels reduces with an increase in the aluminum concentration in the paste. On steel Kh18N9T there is not much reduction in the thickness of the layer. With an increase in the aluminum concentration in the paste, the average

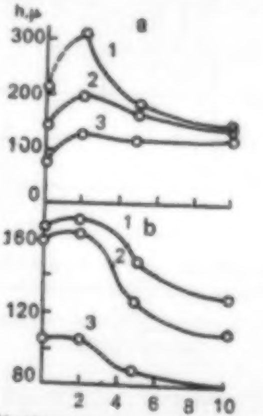

Fig. 31. Variation in thickness of diffusion layer with composition of the mixture during boroaluminizing in pastes:

a—Steel Kh18N9T (1—1200°C; 2—1150°C; 3—1100°C); b—Medium carbon steel (1—1050°C; 2—1000°C; 3—950°C).

surface hardness is reduced: for steel 3 it is reduced from 1750 to 1620 kg/mm^2 (boriding parameters: $t = 1000$°C, $\tau = 3$ h) and for Kh18N9T (1150°C, 1 h)—from 1810 to 1600 kg/mm^2. The external diffusion layer, formed on steels investigated in normal modes of impregnation, are similar to those obtained during boriding.

Boroaluminizing of steels can also be carried out by rapid electric heating [275].

Boroaluminizing by an electrolytic method can be carried out in melts of Al_2O_3–B_2O_3 and Na_2O–B_2O_3–Al_2O_3 systems or in melts of quasi-binary systems: $Na_2B_4O_7$–$NaAlO_2$ and $Na_2B_4O_7$–Al_2O_3 [80, 82, 128]. From practical considerations the last two systems are more suitable.

Electrolytic boroaluminizing is carried out in the temperature range of 900–1050°C. The lower temperature is limited by the increase in viscosity of the melt and the upper by the melting of the steel surface being impregnated.

The zones of deposition of boron and aluminum, depending on the melt composition ($Na_2B_4O_7$–$NaAlO_2$ system) and the parameters of electrolysis are given in Fig. 32. The continuous lines on the plot for the phases formed at different current densities and bath compositions correspond to a processing temperature of 1050°C and the broken lines to 950°C. Three zones can be identified on this plot. In the first (1) zone, a diffusion layer is not formed. In the second (2), on the cathode, only boron is deposited and in the third (3) zone both boron and aluminum are deposited.

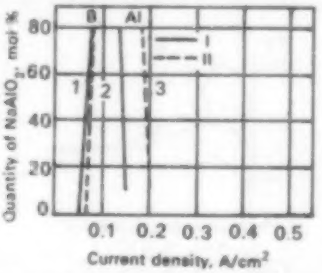

Fig. 32. Phases formed at different current densities and mixture compositions during electrolytic aluminizing:

1—no layer formation; 2—boriding; 3—boroaluminizing (I—$t = 1050$°C; II—$t = 950$°C).

Melts containing more than 50% (mol) $NaAlO_2$, are characterized by a high viscosity and are not very suitable for practical applications. Various liquefying agents such as oxides and salts of alkali metals are added to such melts in order to increase their fluidity and electrical conductivity.

The compositions of some of such officially accepted melts of this type are given in Table 8.

Table 8

Melt No.	B : Al ratio	Melt composition for boroaluminizing, wt.%		
		$Na_2B_4O_7$	Al_2O_3	$Na_2O \cdot K_2O$
I	4 : 6	18	27.5	54.5
II	1 : 1	19.9	20.1	60.0
III	6 : 4	29.4	19.6	51.0
IV	7 : 3	41.6	12.2	48.2

On boroaluminizing in the melts given in Table 8, the thickness of the diffusion layer at the same B : Al ratios and under identical conditions of impregnation is significantly higher than that obtained in melts based on a quasi-binary system such as $Na_3B_4O_7$–$NaAlO_2$. Therefore, all further investigations were carried out using only these melt compositions.

As in the preceding case, an increase in cathode current density above 0.4 A/cm² is not expedient, as this does not ensure any improvement in the thickness of the diffusion layer (Fig. 33).

The effect of the ratio of boron and aluminum (in the melt composition) on the thickness and constituent phases of the diffusion layer is shown in Figs. 34 and 35.

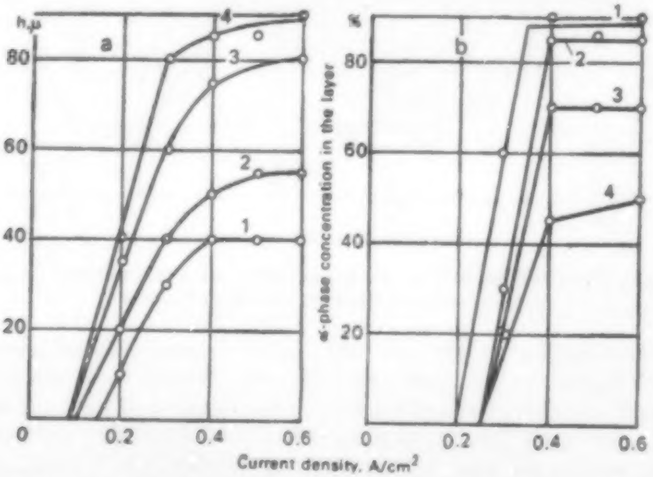

Fig. 33. Effect of current density on (a) constituent phases and (b) thickness of the boroaluminized layer at 1050°C, τ=0.5 h:

1, 2, 3, 4—melts, I, II, III and IV (from Table 8).

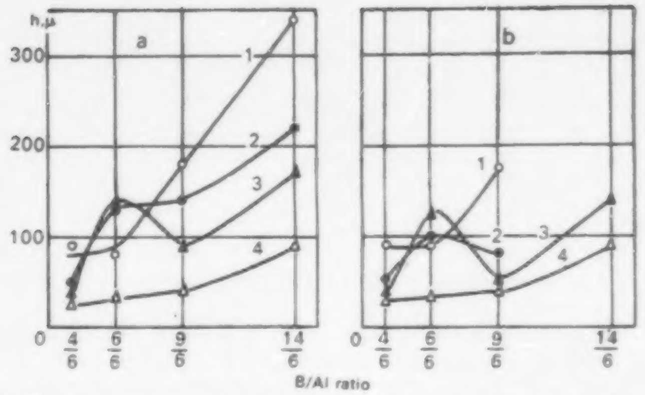

Fig. 34. Variation in thickness of boroaluminized layer on (a) Armco iron and (b) steel 45 depending on B/Al ratio in the melt:

1—1050°C; 2—1000°C; 3—950°C; 4—900°C ($\tau = 4$ h).

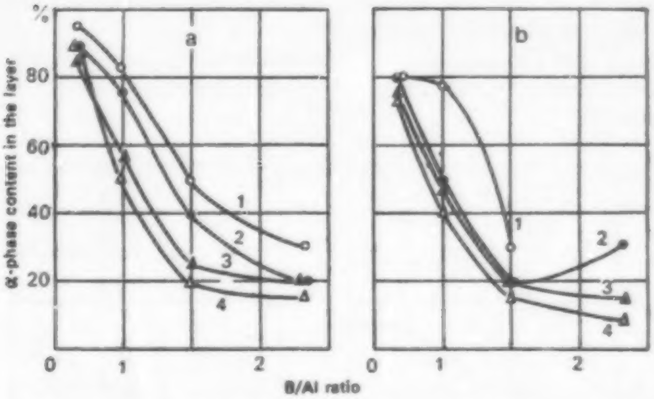

Fig. 35. Effect of B/Al ratio in the melt on composition of constituent phases of boroaluminized layers. (Legend as in Fig. 34.)

Curves obtained at 950° and 1050°C are of a complex optimal type. The maximum obtained for melt II, most probably corresponds to the optimum combination of boron and aluminum for impregnation of steel; the amount of aluminum is sufficient for intensive diffusion and narrowing of the γ-region of iron while, at the same time, boron in the diffusion layer is enough for the formation of a significant quantity of boride phase. As the rate of diffusion of boron in the γ-phase is high as compared to that in the γ-phase, it accelerates its supply to the boundary of the diffusion layer, and the formation of a significant quantity of boride inclusions below the γ-phase layer increases the aggregate thickness of the diffusion layer.

At higher or lower B : Al ratios, only one of the structural constituents is predominant.

Relative quantities of boride phases and α-solid solution at extremal points correspond to 30–45 and 55–70%, respectively.

A further increase in thickness of the layer with a rising concentration of boron in the melt (on variation of the B : Al ratio) is related to its high rate of diffusion as compared to that of aluminum. In the case of steel U8, and at a higher ratio of B : Al, surface melting is also observed in steel 45, which is related to the formation of a complex eutectic in the diffusion layer.

During boroaluminizing in melts I, III and IV, there is a monotonic increase in the thickness of the diffusion layer with an increase in temperature and duration of impregnation in all the steels investigated (Fig. 36). However, it is clear that the exponential and parabolic laws of growth of the diffusion layer are not applicable in this case. The parabolic laws are characteristic for diffusion coating in melt II (Fig. 36b). The variation in thickness of the diffusion layer with temperature in this case is clearly of an optimal type.

The variation in the ratio of boron and aluminum, diffusing in steel with change in temperature, is one of the possible reasons for the deviation from the optimal character of the curve.

An increase in the coating temperature causes a broadening of the aluminized zone in a boroaluminized layer. This rule is especially characteristic for melts II and III. It is not as typical for melts I and IV, as the structure of the diffusion layer in the first case is closer to that obtained for 'pure' aluminizing and, in the latter case, to boriding.

No significant variation in the ratio of borided and aluminized zones was observed during investigations on the effect of the hold on the constituent phases in the diffusion layer. However, on increasing the holding period a variation in the distribution of boride needles was observed: the latter migrate from the aluminized zone to the interface with the substrate metal. Naturally, this variation in relative positions between the boride and the α-phase in the frontal zone of diffusion cannot but influence the rate of growth of the layer.

For simultaneous diffusion saturation of carbon steels with boron and carbon using a gaseous phase, Slavin and Moskvin [273] used aluminothermic ferroboron powder 14.67% B, 15.2% Al, 2.75% Si, 0.8% C) with a particle size of 0.5 to 3 mm. Boron and aluminum were transformed to chlorides in a special reactor. Hydrogen chloride was introduced into the working chamber of the furnace after passing through ferroboron heated up to 950–1100°C. Specimens were placed in a metallic shell. The optimum flow rate of the gas was found to be 50 cm^3/min.

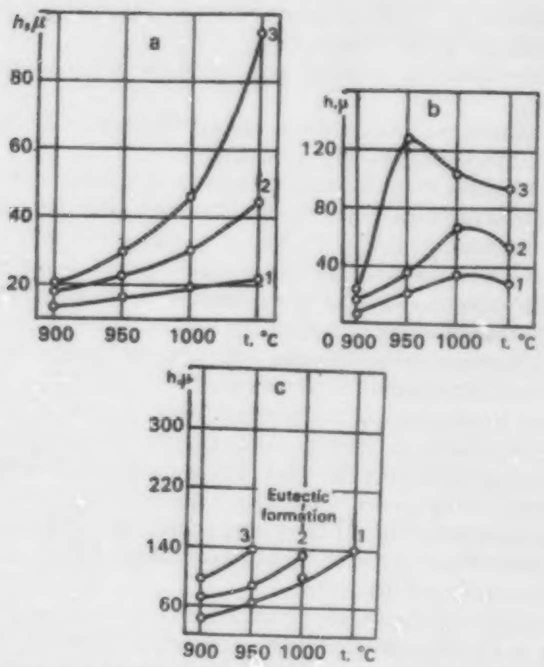

Fig. 36. Effect of temperature on thickness of diffusion layer during electrolytic boroaluminizing of steel 45. Melt I—a, II—b, IV—c (Table 8), Current density 0.3 A/cm^2. Duration of impregnation:

1—1 h; 2—2.5 h and 3—4 h.

The effect of temperature on the thickness of the diffusion layer is shown in Table 9.

The external part of the diffusion coating consists of ferrite alloyed with boron and aluminum. Boride phase is distributed along the interface of the α-phase and the substrate metal. According to the authors of [273], a formation of boron carbide at the interface with the substrate metal is possible in steel U10, which in our opinion seems less probable.

Table 9

Temperature, °C	950	1000	1050	1100
Thickness of boroaluminized layer, (3.5 h, steel 40)	183	336	390	425

As stated earlier, the structure of the boroaluminized layer is determined by the method of diffusion coating employed, the composition of the active mixture, the temperature and duration of treatment and also by the quality of the steel substrate. In spite of the diversity in diffusion-layer structures obtained under different conditions, it is possible to tentatively classify them in three wide categories:

I—Boroaluminized layer externally differs very little from the borided layer and has a typical acicular structure (Fig. 37, a). This type of boroaluminized coatings is formed in impregnating mixtures with higher concentrations of aluminum (or other aluminum-bearing materials). In such cases aluminum does not form an independent phase with iron, but dissolves in

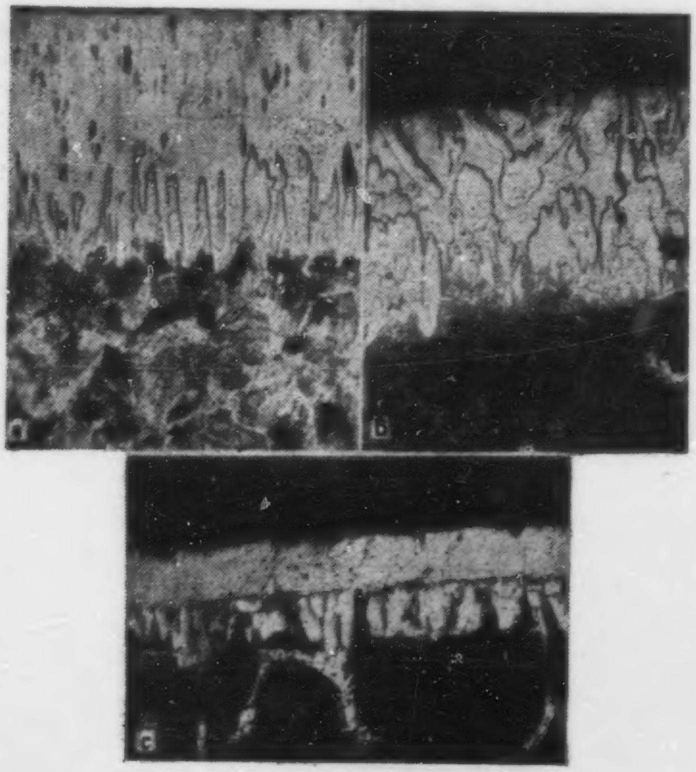

Fig. 37. Microstructure of electrolytic boroaluminized coatings on steel 45 (×300):
a—surface impregnation, preferentially with boron; b—with boron and aluminum; c—impregnation preferentially with aluminum.

moderate amounts in borides of iron or structural defects of the layer (for example, along the boundaries of boride needles).

II—A boroaluminized layer is a conglomerate of boride and aluminide phases: irregularly rounded borides are randomly distributed in the aluminized layer (Fig. 37, b).

Depending on the potential of the diffusion source of aluminum, the base for such a coating could be α-phase, i.e. solid solution of aluminum and boron in α-iron (for examples as in the case of electrolytic methods of boroaluminizing investigated) or aluminides of iron (generally Fe_2Al_5), superlattice structures ($FeAl$ and Fe_3Al) and α-solid solution, alloyed with boron, progressively substituting each other.

In such cases, the potential of the diffusion source for aluminum as well as for boron should be sufficiently high.

III—Most of the layer is composed of aluminides consisting of: α-phase, superlattice + α-phase or aluminides of iron (generally Fe_2Al_5) + superlattice + α-phase (depending on the potential of the diffusion source of aluminum). The borided zone, representing the smaller part of the layer in this case, is distributed preferentially at the interface between the aluminized layer and the base metal (Fig. 37, c). These types of diffusion layers are formed in the case of a clear predominance of the aluminum-bearing component in the mixture.

The borided zone in layers of type I may have one (Fe_2B) or even two borides of iron ($Fe_2B + FeB$). In layers of types II and III, the borided zone contains only Fe_2B.

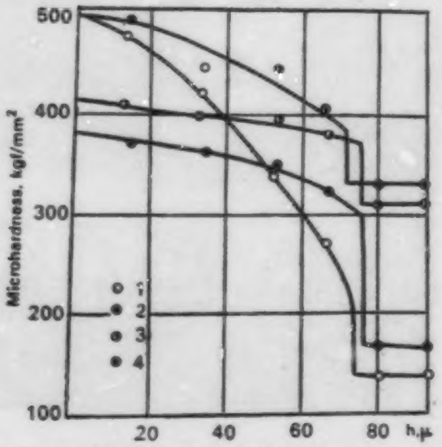

Fig. 38. Variation in microhardness along depth of α-solid solution in boroaluminized layers on (1) Armco iron, (2) steel 20, (3) steel 45, and (4) steel U8: $t = 1050°C$; $\tau = 4$ h, melt I (Table 8).

These three types of structures cover practically all cases of formation of boroaluminized diffusion coatings on plain carbon and low-alloy steels. It is precisely these materials which are most commonly subjected to boroaluminizing.

The microhardness of individual structural constituents of boroaluminized coating produced by using different impregnation techniques has already been indicated. The variation in microhardness along the depth of the aluminized part of a boroaluminized layer, obtained by electrolytic impregnation is shown in Fig. 38. A similar dependence has also been observed in other boroaluminizing processes in the case of an identical structure of the layer (type III layer).

The microhardness of boride, Fe_2B, (Fig. 39) increases with increase in aluminum-bearing constituents in the impregnating mixture. Most investigators have attempted to explain this by the dissolution of aluminum in the boride phase [24, 270, 271]. In plain carbon steels, the microhardness of Fe_2B can vary in the range of 1350–1400 to 1680–1750 kgf/mm².

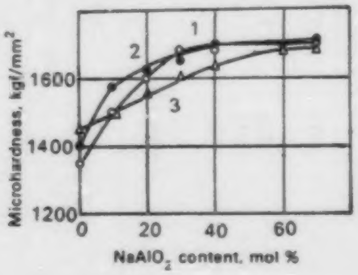

Fig. 39. Effect of $NaAlO_2$ content in a melt on microhardness of boride, Fe_2B, in boroaluminized diffusion layer on (1) Armco iron (2) steel 45 and (3) steel U8: ($t = 1000$°C, $\tau = 3$ h).

The effect of boroaluminizing using pulverized ferroalloys on the mechanical properties of steel 45 can be seen from Table 10 [276].

Boroaluminized steels have a high wear resistance which is, in many cases, higher than the wear resistance of borided steels. Data on the wear resistance of steel 10 and steel U8, boroaluminized in a mixture mainly consisting of aluminum and boron carbide, is given in Table 11 [271].

Similar results were obtained for the wear resistance of boroaluminized coatings obtained by diffusion saturation in pastes (Table 12) [274] and by using the aluminothermic process of boroaluminizing (Table 13).

Abrasion resistance was determined according to the method developed at the Institute of Energetics and Electrotechnology, Academy of Sciences, Latvian SSR, based on friction against moving abrasive band [277]. The rate

Table 10

Diffusion coating	Thickness of diffusion layer on steel 45	σ_v	σ_t	δ	ψ	a_H	σ_{-1}	σ^x_{-1}
		kgf/mm^2		%		kgf/cm^2	kgf/mm^2	
Untreated	—	61.0	34.00	25.0	52.5	4.5	27.0	5.0
Boroaluminized:								
30% Al	0.80	60.0	28.5	10.0	28.0	9.5	24.0	5.0
70% Al	0.90	60.5	28.0	6.0	3.5	3.5	28.5	13.0

Table 11

Coating	Mixture composition, wt. %	Layer thickness, μ		Relative wear resistance	
		Steel U8A	Steel 10	Steel U8A	Steel 10
B	$84 B_4C + 16 Na_2B_4O_7$	200	240	4.4	4.2
B–Al	$85 (84 B_4C + 16 Na_2B_4O_7) + 15 (97 FeAl + 3 NH_4Cl)$	200	217	4.48	4.35
B–Al	$75 (84 B_4C + 16 Na_2B_4O_7) + 25 (97 FeAl + 3 NH_4Cl)$	188	210	3.3	3.0
B–Al	$50 (84 B_4C + 16 Na_2B_4O_7) + 50 (97 FeAl + 3 NH_4Cl)$	140	190	0.9	0.87
Al	$97 FeAl + 3 N_4Cl$	270	310	0.5	0.48

Table 12

Type of steel	Boro-aluminizing regime	Wear, mg/cm² h, at $\tau_{test}=30$ h				Untreated base material
		Al content in the paste, %				
		0	2	5	10	
Steel 3	1000°C, 3 h	0.040	0.038	0.035	0.044	0.258
1Kh18N9T	1150°C, 1 h	0.048	0.040	0.033	0.032	0.132

Table 13

Diffusion coatings on steel 45 (aluminothermic method)	Impregnating regime		Relative wear	
	t, °C	τ, h	During abrasive wear	During sliding friction without lubrication
B–Al	1000	4	2.71	2.85
B	1050	4	2.85	2.4

Note: Hardened and low temperature tempered specimen of steel 45 was used as standard.

of sliding was 30 m/min, and load was 10 kgf/cm². The wear was estimated from the loss of weight during testing and the length of the friction path.

High wear resistance of boroaluminized steels during sliding friction has been reported by Paseohnic et al. [82]. The wear resistance was measured on an MFT-1 friction machine. Tests were carried out in pairs, with Br. OTsC5-5-5 bronze at a sliding rate of 0.1 m/s. Commercial grease USS with 10% of a quartz sand was used as lubricant and was uniformly applied after every 100 m of the path.

The extent of wear of boroaluminized steel 45 is 4–6 times less than that of improved steel (HRC 26–28). The wear of bronze in friction with boroaluminized steel 45 is 2–4 times lower than that for friction with steel 45. Borochromizing reduced the coefficient of friction by 16%.

In the authors' investigations, a high wear resistance of boroaluminized steel 45 was observed under conditions of dry sliding friction (Table 13). Tests were carried out on an MI-type machine at a sliding speed of 1.0 m/s, with a load of 10 kgf/cm² and a test duration of 2 h. For purposes of comparison, a disk of steel R18 (HRC 62) was used as a standard. However, in most cases the boroaluminized layer was not better than the borided layer in respect of wear resistance.

Boroaluminizing in pulverized mixtures with a high aluminum content is known to considerably increase the endurance limit and corrosion fatigue limit (Table 10) [276].

A high thermal stability of boroaluminized carbon steels has been noted in many reports [21, 65, 271, 274, 278 and others]. Data on the heat resistance of plain carbon steel, boroaluminized by using various techniques is given in Tables 14–16. The thermal stability of carbon steels, boroaluminized using a gas process, and tested at 900 to 1000°C for 100 h, was found to be 40 to 45 times higher than the original material [273].

Table 14

Temperature of testing heat resistance, °C	% gain in wt. ($\tau_{test} = 2$ h)			
	Steel 1		Steel ShKh15	
	untreated	boroaluminized	untreated	boroaluminized
500	0.036	0.049	0.005	0.016
600	0.128	—	0.006	0.023
700	0.714	0.098	0.240	0.264
800	3.520	0.430	0.930	0.352

Table 15

Diffusion coating	Conditions of aluminothermic impregnation		wt. gain at 1000°C, 26 h, g/m^2			
	t, °C,	τ, h	Commercial grade iron	Steel 20	Steel 45	Steel U8
Base metal without coating	—	—	1454	1310	1395	1100
B–Al	1100	8	20.8	34.1	41.8	33.4
B	1100	8	18.0	32.0	17.0	31.0

Thus on boroaluminizing the thermal stability increases by 30 to 70 times depending on the process employed for boroaluminizing. However, this dependence is weaker than that observed in the case of 'pure' aluminizing. Data on the kinetics of oxidation of boroaluminized carbon steels is given in Fig. 40.

Table 16

Grade of steel	Boroaluminizing regime in paste	wt. gain, mg/m² h at 700°C, 100 h				Base metal without coating
		% Al in paste				
		0	2	5	10	
1Kh18N9T	1150°C, 1 h	60	48	42	35	210
Steel 3	1000°C, 3 h	224	200	146	105	2410

A still more promising application of boroaluminizing is for the improvement of the thermal stability of special high-temperature creep-resistant steels and alloys [22, 279].

A boroaluminized ZhC6K alloy has a higher heat resistance than a corresponding one-component diffusion coating [22].

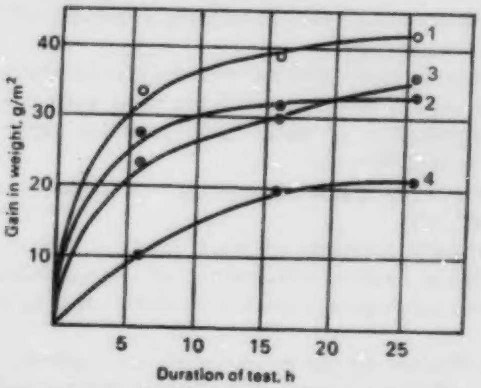

Fig. 40. Heat resistance of an aluminothermic boroaluminized layer (testing temperature 1000°C), on (1) Armco iron, (2) steel 20, (3) steel 45, (4) steel U8. Impregnating regime $t = 1000$°C, $\tau = 8$ h. Mixture composition: 70% Al_2O_3 + 30% (40% B_2O_3 + 60% Al) against 0.5% NaF.

The highest thermal stability is that of a diffusion layer obtained in mixtures containing 70–80% of Al and 20–30% of B. Microstructural studies indicate that the structure of the layers in these cases are similar to those obtained after aluminizing. Chemical analysis reveals that the surface layer contains 50% of Al and 5% of B. After testing for thermal stability, the thickness of the coating increases by a factor of 1.5 in the case of the best combination of a two-component-coating and by a factor of two for an aluminized coating. Thus, introduction of boron in small amounts in an aluminized layer reduces the rate of resorption of the layer at higher temperatures.

Naturally, the thermal stability of a coating depends not only on the composition of the impregnating mixture but also on the conditions of surface impregnation. The following conditions have been found to be optimum for obtaining thermally stable boroaluminized diffusion layers by diffusion saturation techniques: $t = 900°C$, $\tau = 2$ h; 20% metallic component (the active mixture comprises the metallic component, an activator (5% NH_4Cl) and an inert component (Al_2O_3). The thickness of the diffusion layer so obtained should be about 70 μ.

Boroaluminized diffusion coatings obtained under such conditions have a 2–3 time higher thermal stability than the aluminized layers and are more stable at high temperatures. These conclusions drawn with regard to the optimum mixture composition were checked by conducting tests at 1000 and 1100°C for 400 [279] and 200 [22], respectively.

After testing at 1000°C for 400 h, only some isolated dotted marks of oxidation were observed on the surface of boroaluminized specimens.

However, under identical testing conditions, large areas of disintegration were traced on aluminized layers, penetrating to a depth of 150 at a normal thickness of the coating 650 μ.

A boroaluminized layer, obtained according to the aforementioned technology, has the highest corrosion resistance in an environment of the flue gases during combustion of sulfur fuel containing vapors of sea water [$t = 900°C$, $\tau = 15$ h] [279].

Boroaluminized (by sequential method) steel 40 can resist the attack of liquid aluminum [279].

A high corrosion resistance of boroaluminized carbon steel in a 10% aqueous solution of common salt, caustic soda, hydrochloric, sulfuric and phosphoric acids and in other corrosive mediums has been reported in [271, 280].

The results obtained by our investigations are, however, different (Table 17). From the table it can be seen that a boroaluminized layer disintegrates, not only faster than borided or aluminized layers, but also at rates faster than those for untreated steels. This appears to be natural considering the electrochemical mechanism of disintegration of metals and coatings in liquid mediums. We feel that boroaluminizing is not suitable for obtaining a protective coating on carbon steels in aqueous solutions of salts, alkalies and acids.

As regards our conclusions, based on the properties of boroaluminized steels, it should be remembered that the main aim in the study of boroaluminizing is to formulate a suitable regime for obtaining a diffusion layer that could combine the positive properties of boride and aluminide diffusion coatings, i.e. a high hardness and wear resistance together with a high thermal stability.

From an analysis of the data given above it follows that for practical pur-

Table 17

Coating	Testing medium	Wt. loss, g/m^2 at $t_{test} = 75$ h			
		Commercial grade iron	Steel 20	Steel 45	Steel U8
Untreated	3% NaCl	11.6	5.2	4.5	8.7
B–Al	,,	2.0	6.0	8.0	0.5
B	,,	5.6	10.0	12.0	14.0
Al	,,	4.1	5.6	5.3	5.0
Untreated	10% H_2SO_4	32	76	832	1200
B–Al	,,	2379	4618	1923	2863
B	,,	23	29	23	78
Al	,,	160	47	149	2882
Untreated	30% HCl	592	1766	3543	1389
B–Al	,,	3590	4523	3748	3240
B	,,	185	21	30	19
Al	,,	938	1415	806	1230
Untreated	40% H_3PO_4	43	113	1192	1173
B–Al	,,	2274	1622	2467	4025
B	,,	1226	397	754	420
Al	,,	293	38	356	572
Untreated	10% HNO_3	6128	5748	6070	5720
B–Al	,,	5000	4655	4867	5413
B	,,	1650	1738	1296	1581
Al	,,	2619	2077	2183	2085
Untreated	50% CH_3COOH	42	39	44	42
B–Al	,,	143	152	289	461
B	,,	8	20	25	5.2
Al	,,	52	38	31	45

poses, this aim is not achieved: coatings of type I have a high wear resistance. Their thermal stability is slightly higher than those of boride coatings. Coatings of type III have a high thermal stability but are not different from aluminide coating with a significant improvement in wear resistance.

The slight improvements in the indicated properties do not appear to justify a more complicating technology of diffusion saturation.

In some cases, especially when subjected to impact loading, it should have been possible to recommend the use of a coating of type II (with a view to reduce the brittleness of the borided layer). However, here the highly complex nature of the control on size, form and mutual dispersion of boride particles in an aluminized layer renders it unsuitable.

In our opinion, the only virtue of boroaluminizing, as compared to boriding, is the increase in microhardness and wear resistance of the boride phase and the increase in the rate of surface alloying (for example, in the case of electrolytic boroaluminizing) during the impregnation process in a boriding mode (layer of type I). These advantages are already being exploited. However, these statements do not relate to special alloys and refractory metals. Zemskov et al. [279] have conclusively demonstrated that the properties of a boroaluminized layer of ZhS6K alloy (thermal stability and corrosion resistance) are significantly better than those of the corresponding one-component diffusing coatings. Apparently, the diffusion coatings on similar types of alloys need to be subjected to further systematic investigations.

2. CHROMOALUMINIZING

Diffusion saturation of metals and alloys, simultaneously with aluminum and chromium, is employed to obtain a much higher thermal stability and wear resistance as compared to chromized and aluminized diffusion coating. The search for a suitable process of chromoaluminizing of iron and steel began in the late 30s and continued in the early 40s [281–283]. To date, a large number of investigations have been devoted to chromoaluminizing of plain carbon and alloy steels, nickel-based heat-resistant alloys, titanium alloys and copper, and also to the study of properties of the formed diffusion layers. Reviews of investigations covering these aspects are given in the monographs of Dubinin [101] and Minkevich [284].

Chromoaluminizing is carried out using powders of elements, ferroalloys or a specially prepared chromoaluminizing master alloy [1, 20, 101, 276, 284, 286–288], using aluminothermic mixtures [102, 290, 291] with halide additions forming an active gaseous phase or in a vacuum [291–293], in melts of aluminum with chromium [294] or by drossing [50].

Chromoaluminizing of steel 45 in pulverized systems consisting of ferrochrome and aluminum (60%), ammonium chloride (5%) and aluminum oxide (35%), has been investigated by Pokhmurskii, Dalisov and Brodyak [285]. The aluminum content in the mixture varied between 5 to 40%. It has been established that a simultaneous diffusion of chromium and aluminum in steel takes place only for an aluminum content in the mixture of up to 20%.

The thickness of the diffusion layer on steel increases with an aluminum content in the powder mixture [101, 285]. During this, there is a change in the ratio of chromium and aluminum on the surface as well as in the structure of diffusion layer [101].

Data on the effect of the ratio of ferroaluminum and ferrochromium in the impregnation mixture on the depth of the layer and the concentration of aluminum and chromium on the surface of steel 10 and Kh18N10T after diffusion saturation (at 1025°C and holding period of 10 h) in ferroalloy-base powder mixtures containing 1.5% of ammonium chloride as an additive, is reproduced in Table 18 [101].

Table 18

Steel grade	Mixture composition, %		Layer thickness, mm	Surface concentration, %	
	FeAl	FeCr		Cr	Al
Steel 10	75	25	0.55	6	37
	50	50	0.37	10	22
	20	80	0.23	42	3
Kh18N10T	75	25	0.20	12	38
	50	50	0.22	15	25
	20	80	0.18	33	12

Aluminum diffusing faster than chromium, drives away carbon from the surface layer into the volume and thus hinders the formation of a carbide diffusion layer. The structure of a chromoaluminized layer on steel comprises a solid solution of chromium and aluminum in α-iron. On such a layer, the concentration of chromium and aluminum gradually decreases from the surface to the volume. On surface alloying in mixtures rich in aluminum the constituent phases in the diffusion layer are found to be α-solid solutions of chromium and aluminum, probably with Fe_3Al and FeAl alloyed with chromium.

Simultaneous diffusion saturation of chromium and aluminum takes place in Cr_2O_3 based aluminothermic mixtures, with aluminum concentrations higher than 25%. At lower concentrations of aluminum it is mainly consumed in the reduction of Cr_2O_3 and remains practically inactive during the formation of a diffusion layer.

The effect of aluminum on the thickness of the chromoaluminized layer on Armco iron and steel U8 is shown in Fig. 41. With an increasing aluminum concentration in the mixture, the thickness of the layer also increases. In such a case the concentration of aluminum in the diffusion layer increases, whereas there is a reduction in the concentration of chromium. According to spectrographic analysis, at a 30% aluminum content in the mixture, the diffusion coating on steel 45 consists of 29.3% Cr, and 9.7% Al whereas at a 40% aluminum content the coating contains 2.7% Cr and 33.3% Al.

Data on the effect of Al_2O_3 and AlF_3 additions on the thickness of chromoaluminized layers is reproduced in Fig. 41. At Al_2O_3 concentrations in the mixture below 30%, large buttons of chromium–aluminum alloy are formed during the stage of reduction, thereby reducing the activity of the mixture.

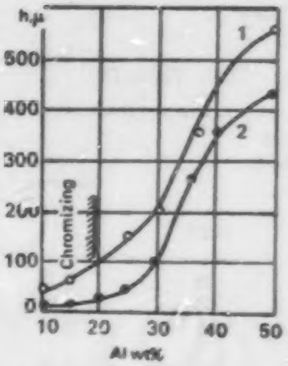

Fig. 41. Variation of thickness of a diffusion layer with mixture composition in case of simultaneous diffusion saturation of steels with chromium and aluminum by aluminothermic method using 30% Al_2O_3, 5% AlF_3 and 2% ammonium chloride in the mixture:

$t = 1100°C$; $\tau = 4$ h.

1—steel E12; 2—steel U8.

Additions of more than 30% aluminum lead to a decrease in the potential of the diffusion source of chromium and aluminum.

Variation in the thickness of the chromoaluminized layer on iron and plain carbon steels based on temperature and duration of impregnation is shown in Fig. 42.

The surface of Armco iron layer thus formed consists of σ-phase, alloyed with aluminum, ordered solid solution of Fe_3Al alloyed with chromium and

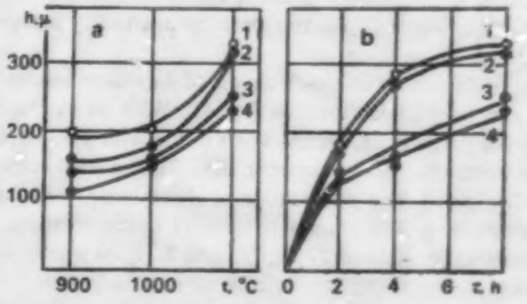

Fig. 42. Effect of temperature and duration of impregnation on the depth of a chromoaluminized layer on (1) Armco iron, (2) steel 20, (3) steel 45 and (4) steel U8. $Cr_2O_3/Al = 70/30$. $AlF_3 = 5\%$, $Al_2O_3 = 30\%$:

a—$\tau = 8$ h; b—$t = 1100°C$.

α-solid solution of chromium and aluminum in iron. On the surfaces of steel 45 and steel U8, in addition to the zone of carbides $(Cr, Fe)_{23}C_6$ and $(Cr, Fe)_7C_3$, zones of ordered solid solution of Fe_3Al alloyed with chromium and α-solid solution of chromium and aluminum in iron are also observed.

A zone of ordered solid solution of FeAl alloyed with chromium is formed on the surface of iron and steels during diffusion saturation in a mixture containing 40% of aluminum.

It can be seen from Fig. 43, that the alloying of medium carbon (0.4%), steel with silicon (up to 1–2%), nickel (up to 2%) and chromium (up to 5%) results in a reduction in thickness of the diffusion layer. The microstructures of chromoaluminized steels 40 and 40Kh5 are given in Fig. 44.

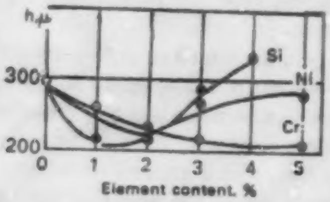

Fig. 43. Effect of alloying elements on the thickness of a chromoaluminized diffusion layer on steel with 0.4% C:

(t=1100°C, τ=8 h).

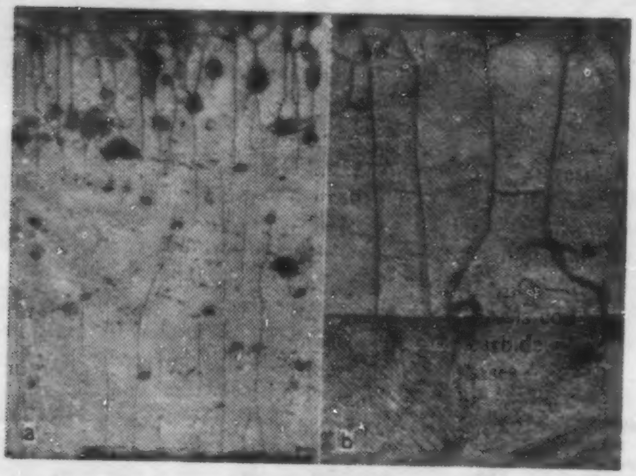

Fig. 44. Microstructures of chromoaluminized layers on (a) steel 40 and (b) steel 40Kh5:

t=1100°C, τ=8 h, ×250).

By a mathematical analysis of the experiments optimum parameters for diffusion saturation (to improve the thermal stability) of iron and plain carbon steels have been established as follows: mixture composition wt.%—100% [37% Al_2O_3 + 63% Cr (63% Cr_2O_3 + 37% Al)] + 4% AlF_3; $t = 1050°C$, duration of the treatment τ—6 h.

Chromoaluminizing of low-carbon steels using a gaseous phase was investigated by Minkevich and Berjgika [283]. The aerosol method has been used by Prosvirinium, Myasoyedevim and Zudinim [295] for simultaneous surface impregnation of iron and austenitic heat-resistant steels with chromium and aluminum. A mixture of powdered aluminum and chromium, treated with concentrated hydrochloric acid together with NaCl and NH_4Cl is introduced in the reaction chamber, consequently producing a vapor-phase medium with suspended solid particles.

The concentration of aluminum and chromium on steel after surface impregnation by the aerosol method was found to be considerably lower than those obtained by diffusion saturation in a mixture of powder elements, ferroalloys and aluminothermic mixtures.

Ferrite diffusion layers, with a gradual decrease in the concentration of chromium and aluminum along the depth of the coating on steel 3 were obtained by chromoaluminizing in a vacuum [292]. An alloy of chromium and aluminum containing—Cr = 67.9%, Al = 20.4%, C = 0.06% and the remainder, iron, was used as the diffusion source of chromium and aluminum. Placed in special trays, the specimens were uniformly covered from all sides, with pieces of the alloy of a size of 3–15 mm. After treatment at 1200°C for 5 h the concentrations of chromium and aluminum at the surface were found to be 45% and 28%, respectively. The thickness of the diffusion layer obtained was 1 mm.

Chromoaluminizing of high-temperature creep-resistant nickel alloys, ZhC6K, EI-867 and EI-929 was studied in [287] with the object of improving their heat-resistant characteristics. Powdered chromium–aluminum alloy, initially roasted in an electric furnace, along with 1–2% of ammonium chloride, was used for simultaneous impregnation with chromium and aluminum. The powder mixture so obtained can be used 4 to 5 times for diffusion coating after which, for every successive impregnation, it is necessary to add 5% of freshly roasted alloy in order to maintain the consistency of results of surface alloying. According to the author, the following mixture compositions are found to be optimal for obtaining good quality surface coatings:

1. 98% CrAl + 2% NH_4Cl,
2. 68% CrAl + 30% Al_2O_3 + 2% NH_4Cl.

At 1000°C and 1100°C a maximum growth rate of the layer is observed during the first 6–10 h after which there is no significant increase in the thickness of the diffusion layer. At 1200°C the rate of growth of the diffusion layer remains fairly high during the first 20 h.

Chromoaluminizing of ZhS6K and EI-867 alloys in mixtures of powder elements has been studied by Zemskov and colleagues [1, 20]. The thickness of the diffusion layer as well as its microhardness at the surface increase with an increase in the aluminum content of the active mixture. Only chromizing of alloys took place at aluminum contents in the mixture below 3%, and, between 3 to 50% Al, chromoaluminizing occurred.

For diffusion saturation of ZhS6K [291–293], ZhS6 and ZhCZLS [291] alloys with chromium and aluminum in a vacuum, pieces of chromium–aluminum of sizes of 10–20 mm (composition—10–25% Al, 2–20% Fe, 0.04–10% C, and the remainder Cr) [291–292] and a powder mixture of the elements along with alumina (44% Cr, 6% Al, 50% Al_2O_3) [293] have been used.

In the case of chromium–aluminum alloys, after treatment at 1180°C for 4 h, a 60 μm thick diffusion layer with concentrations of chromium and aluminum at the surface of 11% and 25%, respectively, was obtained on the surface of ZhS6K alloy. The concentration of aluminum gradually decreased along the depth of the coating. The chromium content at the surface was somewhat lower than that in the volume and at a depth of 30 to 40 μm increased to ~20%. The structure of the surface zone comprises of a complex alloyed γ-solid solution of nickel with a large quantity of dispersed intermetallic phase Ni_3Al (or NiAl). In lower parts of the diffusion layer large carbide inclusions are observed.

According to the data of Kozlova [293] on chromoaluminizing of ZhS6K alloy in a mixture of powder elements and aluminum oxide for 4 h at 1200°C, the diffusion layer obtained consists of NiAl and Ni_3Al phases and zones with increased concentrations of carbides. The aluminum content gradually decreases from 20% at the surface to 10% in the bulk, (at a depth of 120 μm). The maximum concentration of chromium was observed (see also [291] and [292]) and not on the surface, but at a depth of 40 to 80 μm. In the diffusion layer a complex solid solution is observed along with aluminides and carbides.

Simultaneous surface impregnation of steels and other alloys with aluminum and chromium has a significant influence on their mechanical properties, at room temperature as well as at high temperatures on their heat and wear resistance and other service properties.

The microhardness of chromoaluminized layers on steel is relatively low and is of the order of 150 kgf/mm^2 on steel 3 (at aluminum and chromium concentrations of 8 and 6%, respectively) and 320–360 kgf/mm^2 (at 12–15%Cr and 15–24% Al). At smaller concentrations of chromium and aluminum in the surface layer, the mechanical properties of chromoaluminized steel 20 do not significantly differ from those of untreated steel; an increase in chromium and aluminum leads to a reduction in tensile strength and ductility (Table 19) [292].

The microhardness of a chromoaluminized layer on steel 45 increases from 300 to 700–750 kgf/mm^2 on increasing the aluminum content in the

Table 19

Impregnating regime	Tensile strength, kgf/mm^2	Relative elongation, %	Reduction in area, %
Untreated	54.6	26.9	67.2
Chromoaluminized (8–10% Cr, 6–7% Al)	52.3	31.0	63.8
Chromoaluminized (15% Cr, 20% Al)	37.1	9.6	6.5

powder mixture from 5 to 50% and becomes equal to the microhardness of aluminized layers. Chromoaluminizing, as in the case of aluminizing, also reduces the tensile strength and ductility as well as the impact strength of steel 45 with an identical structure at the center obtained on vacuum annealing (Table 20) [276]. Chromoaluminizing decreases the endurance limit, but slightly improves the corrosion-fatigue resistance in a 3% NaCl solution.

Chromoaluminized diffusion coatings on steel U8 produced by the aluminothermic method have a much higher wear resistance during dry sliding friction than tempered steel U8 without a chromoaluminized coating.

Results of tests on heat-resistant properties at 800°, 900° and 1000°C for 100 h (Table 21) confirm the improved protective properties of chromoaluminized layers on Armco iron and steel U8 as compared to chromized and aluminized layers on the same material.

Alloying of medium carbon steels with chromium and silicon improves its heat resistance at 1000°C after chromizing. On the other hand, the introduction of nickel in steel reduces its heat resistance (Fig. 45).

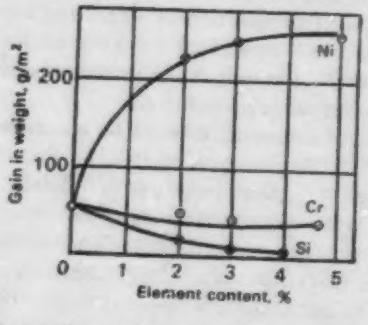

Fig. 45. Effect of alloying elements on heat-resistant properties of chromoaluminized layers on medium carbon steel (0.4% C). Parameters of surface impregnation: $t = 1100°C$, $\tau = 8$ h. Parameters of testing $t = 1000°C$, $\tau = 26$ h.

Table 20

Mode of impregnation of steel 45	Diffusion layer thickness, mm	σ_v	σ_t	δ	ψ	a_H	σ_{-1}	σ_{-1}^k
		kgf/mm²		%		kgf/cm²	kgf/mm²	
Untreated	—	61.0	34.0	25.0	52.5	4.5	27.0	5.0
Chromizing 1100°C, 10 h	0.035 (carbide zone)	52.0	27.5	23.5	52.0	4.0	27.0	14.5
Aluminizing 900°C, 6 h	0.20	58.0	34.0	18.5	17.0	4.1	19.0	—
Chromoaluminizing (5% Al) 950°C, 6 h	0.45	58.5	32.0	25.5	25.0	2.0	17.0	6.0
Chromoaluminizing (10% Al) 950°C, 6 h	0.50	56.5	31.5	17.0	26.5	1.0	15.0	8.0

Table 21

Coating	Chief constituent of the impregnating mixture	t_{test}, °C $\tau_{test} = 100$ h	wt. gain, g/m^2	
			Armco iron	Steel U8
Cr	Cr_2O_3	800	3.7	1.9
		900	5.9	3.7
		1000	Localised failure	
Al	Al_2O_3	800	6.4	7.2
		900	9.4	16.7
		1000	31.6	43.5
Cr+Al	Cr_2O_3+Al	800	3.2	9.6
		900	16.6	20.4
		1000	30.9	39.3

At high temperatures, the protective coating on the surface of plain carbon steel is partly oxidized and partly resorbed. This leads to a reduction in concentration of the impregnating elements in the diffusion layer. As can be seen from Table 22, during heat-resistance testing the decrease in chromium concentration is much sharper than that in aluminum [292]. According to the available data, chromoaluminizing of steel 3 and Kh18H9T is less effective in improving their heat resistance, than chromizing.

Table 22

Material	Testing conditions		Surface concentrations of elements	
	t, °C	τ, h	Cr	Al
Chromoaluminized steel 3	—	—	45.1	26.2
	1000	300	23.4	23
	1000	500	20.6	19.5

Results of heat-resistance tests at 1000°C carried on a variety of steels after chromizing, aluminizing and chromoaluminizing in aluminothermic mixtures are given in Table 23. For steel 20Kh3MVF chromized and chromoaluminized coatings do not provide effective protection against oxidation at 1000°C whereas the protective characteristics of aluminized layers are reasonably good. Chromoaluminizing of steels 2Kh13 and 3Kh19N9MVBT ensure a better heat resistance than chromized and aluminized layers. Chromizing on steel Kh25T and aluminizing on steel Kh18N9T provide more effective protective coatings than chromoaluminizing.

Table 23

Base material	Coating	Wt. gain, g/m^2 during testing time, h							
		6	26	46	66	86	100	120	150
20Kh3MVF	Cr	6.2	12.0	16.8	31.1	80.6	155.9	Coating fails	
	Al	14.2	26.5	30.1	33.6	38.0	40.1	44.2	46.4
	Cr+Al	31.0	32.1	80.9	13.74	1714	1937	Coating fails	
2Kh13	Cr	6.9	10.9	22.1	25.4	32.3	35.2	38.3	44.9
	Al	27.4	59.0	64.3	66.7	70.2	72.0	90.9	106.5
	Cr+Al	6.9	10.3	13.8	16.1	19.4	20.7	25.2	35.9
Kh25T	Cr	4.7	11.9	14.4	17.4	19.3	20.7	29.2	38.0
	Al	10.4	26.2	42.5	53.3	61.2	66.8	72.1	90.9
	Cr+Al	5.6	15.3	22.2	27.2	29.1	30.6	37.9	45.8
Kh18N19T	Cr	12.7	16.8	28.4	34.9	40.3	43.9	47.7	54.1
	Al	10.1	19.4	21.0	24.2	29.2	31.4	34.8	40.3
	Cr+Al	10.5	19.9	25.0	29.1	34.3	36.1	38.2	46.3
3Kh19N9MVBT	Cr	7.1	29.3	44.0	63.8	82.1	97.3	106.1	114.4
	Al	10.0	21.6	31.3	40.6	54.3	64.2	74.1	84.2
	Cr+Al	3.2	7.5	15.6	22.7	23.1	27.4	41.6	47.6

Thus, simultaneous diffusion impregnation of different grades of steels with chromium and aluminum, in some cases, results in a much higher heat resistance as compared to that exhibited by one-component coatings. Apparently, for every steel, it is necessary to select the optimum process parameters ensuring maximum heat resistance under the given conditions of testing. The selection of the parameters for a heat-resistant coating can be carried out by mathematical modeling and optimization of experiments.

Chromoaluminizing is recommended in the manufacture of blades of stationary gas turbines, parts of exhaust systems of engines, heat pipes, combustion chambers and other components made of austenitic steels in such systems where, in addition to good mechanical properties at working temperatures, it is desirable to ensure an improved heat and erosion resistance and a high thermal-shock resistance [101, 284, 295].

The effect of chromoaluminizing on the mechanical properties of nickel alloys has been investigated [291, 292]. Variation in the microhardness in the depth of the diffusion layer is determined by the distribution of impregnating elements [292]. The microhardness of the layer close to the surface is found to be ~600 kgf/mm^2 and decreases sharply toward the center.

Chromoaluminizing at 1180°C for 4 h, followed by annealing to remove the residual tensile stress on the surface, improves the tensile strength of ZhS6K alloy at 975°C, but reduces its ductility (Table 24) [291, 292]. As compared to aluminizing, simultaneous impregnation with chromium and aluminum provides a still higher strength with a considerable reduction in ductility.

Tests for creep resistance have established the favorable effect of annealing at 950°C for 6 h after chromoaluminizing. Such a treatment significantly improves the average time before failure of specimens $\sigma = 20$ kg/mm^2 without influencing the minimum time before failure. Annealing at 1210°C for 3.5 h

Table 24

Diffusion coating regime and heat treatment of ZhS6K alloy	Tensile strength, kgf/mm^2	Percentage elongation, %	Percentage reduction in area, %
	$t_{test} = 975$°C		
Untreated alloy (heat treatment according to technical specifications)	60	4.1	5.4
Chromoaluminizing at 1170°C for 4 h +annealing at 950°C for 6 h	70.2	3.8	3.8
Chromoaluminizing at 1180°C for 4 h +annealing at 1210°C for 3.5 h	71	3.8	3.8
Aluminizing at 870°C for 30 h +annealing at 950°C for 6 h	56.5	5.0	7.25

after chromoaluminizing and also aluminizing followed by annealing for 6 h at 950°C lead to a reduction in the life on the specimen (Table 25) [291].

Presman et al. [291] have also reported that chromoaluminized ZhS6K alloy has a much higher fatigue strength at working temperatures than aluminized alloy.

Table 25

Surface impregnation and heat treatment regimes	Time before failure at $\sigma = 20$ kgf/mm^2, 950°C, h
Untreated alloy (standard heat treatment specifications)	53.97* (50.0–58.83)
Chromoaluminizing, 1170°C, 4 h	42.0* (38.51–46.83)
Chromoaluminizing, 1170°C, 4 h +annealing at 950°C for 3.5 h	70.35* (49.0–81.35)
Chromoaluminizing, 1170°C, 4 h +annealing at 1210°C for 3.5 h	32.21* (25.51–40.0)
Aluminizing, 870°C, 30 h +annealing at 950°C for 6 h	42.25* (36.08–77.0)

*Mean values.

Results of full-scale trials at 750°C on turbine blades for VK-1A engines made of KhN77TYuR (E1-473B alloy), chromoaluminized in a vacuum, are given in [296]. Testing showed that after undergoing chromoaluminizing, turbine blades became more uniform in respect of toughness. This improvement in toughness has been attributed to the elimination of nonuniformities (which are observed after cutting and polishing operations) in the surface layer of the blade as a result of diffusion saturation. In addition, the reduction in the endurance limit under service conditions is much lower in the case of chromoaluminized blades than that for untreated blades. With an increased service life, the merits of chromoaluminized blades are quite obvious.

The chromium content on the surface of a chromoaluminized blade remained practically unchanged after 1200 h of use. The aluminum content, however, was reduced from 12–15 to 9%. Consequently, the surface layer of the blade contained a sufficiently large amount of chromium and aluminum which ensured a long (more than 1600 h) and reliable performance of the blade in the engine.

Even during heat-resistance tests at 980°C, the surface concentrations of chromium and aluminum were found to decrease on chromoaluminized ZhS6K alloy [292]. Generally, there was a sharp decrease in aluminum concentration, from 26 to 10.4% within 800 h, while the chromium content decreased from 12.2 to 9.0% during this period.

Many authors [101, 291, 292 and others] agree that chromoaluminized diffusion coatings on nickel alloys are more effective in improving their heat resistance than aluminized coatings. For example, according to the data given in [291, 292], chromoaluminized specimens of ZhS6K alloy have a 15 to 20% higher heat resistance at 980°C than aluminized specimens.

After chromoaluminizing and annealing at 950°C for 6 h, and at 1210°C for 3 h, ZhS6K alloy has a better thermal-shock resistance than chromoaluminized and untreated specimens which have been subjected to the standard heat treatment [291].

Thus, nickel-base heat resistance alloys with chromoaluminized coatings can be used in the production of turbine blades and other vital components of gas turbines.

3. ALUMINOSILICONIZING

Materials such as plain carbon and alloy steels [102, 297–300], nickel-base creep-resistant alloys [50, 289, 301–304, 312], refractory metals and their alloys [294, 307–310] and also copper [286, 305, 306] are subjected to simultaneous diffusion saturation with aluminum and silicon. The aim in aluminosiliconizing is to obtain an improvement in the heat-resistant qualities of metals and alloys.

Some methods which have been developed and used in industry are impregnation in a mixture of powder elements or ferroalloys [289, 297, 302–304, 307, 308] and in aluminum–silicon-base melts [294, 299, 300, 309, 311]. Other methods of aluminosiliconizing investigated at the laboratory level are: the powder method [102], impregnation in ferroalloy-base pastes [50, 299] and a number of gaseous-phase methods [297, 312].

Aluminosiliconizing of iron in powder mixtures of elements has been attempted [297] in order to obtain an α-solid solution of silicon and aluminum in iron.

For aluminosiliconized coatings by powder methods, aluminothermic mixtures can also be used where silica (roasted bentonite) serves as the source of silicon [102]. The aluminum content in such mixtures should be more than that required for the reduction of silica. In addition, the mixture also contains alumina and sodium fluoride.

The effect of the aluminum silica ratio on the depth of the diffusion layer on Armco iron and steel 45 is shown in Fig. 10 (e). This dependence is complex. Up to a 20% aluminum content in the mixture pure siliconizing takes place. An increase in the thickness of the diffusion layer with an increase in aluminum content in the mixture is related to the increased quantity of reduced silica and, consequently, the higher potential of the diffusion source of silicon. It should be noted that the thickness of the diffusion layer increases mainly due to the formation of α-phase (composition Fe_3Si) on the surface in which the diffusion mobility of silicon is very high. During this there is no appreciable change in the thickness of the layer consisting of solid solution of silicon in α-iron.

An increase in the aluminum content of the mixture beyond 20% results in the formation of a two-component diffusion layer. Reduction in the thickness of the diffusion layer on transition from a siliconized to an aluminosiliconized layer is attributed to the formation of a ternary α-solid solution on the surface. Further increase in the aluminum content of the mixture favors an increase in thickness of the diffusion layer, probably due to the rise in potential of the diffusion source of aluminum and the formation of an iron-aluminum superlattice. A variation of between 1 to 4% in the sodium fluoride content in the mixture does not have any significant effect on the thickness of the aluminosiliconized layer.

The effect of temperature and duration of treatment on the thickness of aluminosiliconized diffusion coatings, obtained in a mixture of the composition given below is shown in Fig. 46:

$$98\%\,[50\%\ Al_2O_3 + 50\%\,(70\%\ SiO_2 + 30\%\ Al)] + 2\%\ NaF.$$

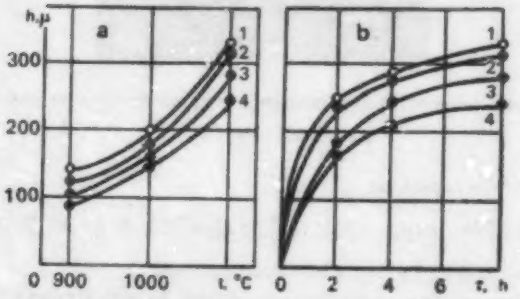

Fig. 46. Effect of temperature and duration of impregnation on thickness of an aluminosiliconized coating on (1) Armco iron, (2) steel 20, (3) steel 45 and (4) steel U8:

a—$\tau = 8$ h; b—$t = 1100$°C.

On diffusion saturation in such a mixture, aluminide Fe_2Al_5, was alloyed with silicon, ordered solid solutions of FeAl and Fe_3Al also alloyed with silicon and an α-solid solution of aluminum and silicon in iron, are formed on the surface of Armco iron, steel 45 and steel U8. The concentrations of silicon and aluminum on the surface were found to be 14.5% and 39.4%, respectively (data of spectrographic analysis). In the zone of α-solid solution of silicon and aluminum in iron, precipitation of a phase of unknown composition takes place on the surface of steel 45 (Fig. 47).

By mathematical modeling and optimization of experiments, the following treatment parameters were found most suitable for obtaining heat-resistant coating by diffusion impregnation on Armco iron and steel U8.

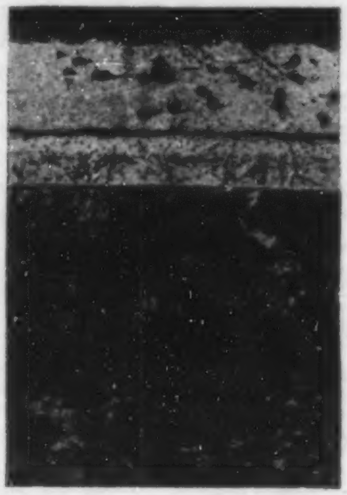

Fig. 47. Microstructure of aluminosiliconized coatings on steel 45: $t=1000°C$, $\tau=8$ h ×200.

Mixture composition, wt.%:

$$97\%\,[50\%\,Al_2O_3+50\%\,(65\%\,SiO_2+35\%\,Al)]+3\%\,NaF,$$

temperature—1000°C, duration of treatment—6 h.

Simultaneous surface impregnation of steel 20 with silicon and aluminum in pastes has been investigated by Kidin et al. [298]. The paste contained Al_2O_3 and NH_4Cl in addition to ferroalloys. Hydrolyzed ethyl silicate was used as binder.

Specimens coated with a paste of the following composition: 44% FeSi (75% Si), 44% FeAl (50% Al), 10% Al_2O_3 and 2% NH_4Cl were heated in an electric furnace ($V_H=1$ deg/s) and by resistance heating ($V_H=50$ deg/s). On heating at the rate of 1 deg/s up to 1100°C and 1200°C, without soaking, 10 and 26 μ thick layers were formed on the surface of steel 20. On impregnation at identical temperatures and after soaking for 5 min, much thicker coatings with lower concentrations of the impregnating elements were obtained by resistance heating. The aluminum and silicon concentrations were gradually reduced from the surface to the volume while, all along the depth the concentration of aluminum was found to be three times higher than that of silicon.

Apparently, the diffusion coating consisted of solid solutions of aluminum and silicon in iron (~10% of Al and ~3% of Si on the surface). With an increase in the treatment temperature the growth of the aluminosiliconized layer was hastened, but, the surface quality deteriorated.

Impregnation of sheet steel with aluminum and silicon in melts of aluminum with 3–11% of Si at 700°C for 35–14 s has been investigated by Aksenova et al. [299, 300]. A good quality coating was obtained by a preliminary treatment at 900–950°C in an atmosphere of cracked ammonia.

On introduction of silicon in the melt, the thickness of the intermetallic layer decreases from 20–25 to 2–5 μ and the structure of the diffusion layer is altered. At 6–7% of silicon a multi-phase diffusion layer is formed on the surface of steel. Thin laminates of Fe_2Al_5, $FeAl_3$, and FeSi are observed below the surface layer consisting of α-solid solution of silicon and aluminum in iron.

Gas-phase aluminosiliconizing in an atmosphere of halides of silicon and aluminum has been studied in [297]. The diffusion layer consisting of α-solid solution of aluminum and silicon in iron with aluminum and silicon concentrations on the surface ~15 and 2%, respectively, was formed on the surface of iron after impregnation at 950°C for 45 min.

Diffusion saturation of nickel alloys in mixtures consisting of powdered aluminum, silicon, alumina and sodium fluoride has been studied [289, 301–304]. According to the data of Zemskov [289, 302–304], the structure of siliconized diffusion coatings on ZhS6K alloy consists of a fine disperse solid solution with silicides of nickel and chromium. The microstructure of aluminized layers does not differ much from those obtained by diffusion saturation with silicon and consist of a fine-disperse mixture of solid solution and aluminides of nickel. It is not, therefore, possible to distinguish between the siliconized, aluminosiliconized and aluminized zones only on the basis of a microstructural examination.

Investigations on microhardness along the thickness of the layer, chemical analysis of surface layer and x-ray structural analysis have shown that simultaneous diffusion saturation with silicon and aluminum takes place under the following conditions: at 900°C, in mixtures containing 10–90% of Si and 90–10% of Al and at 1000°C in mixtures containing 20–70% of Si and 80–30% of Al [289]. In aluminosiliconized diffusion layers, the concentrations of silicon and aluminum are found to be 4–7% and 45–50%, respectively. Near the surface of aluminized and aluminosiliconized diffusion layer Ni_2Al_3 and NiAl phases are predominant and, in the deeper parts, NiAl and Ni_3Al phases. Silicon is present in the diffusion layers in the form of silicides of chromium, tungsten, and titanium [289].

On surface alloying at 900°C the thickness of the diffusion layer gradually increases with increase in aluminum content of the mixture. Similar plots drawn for impregnation at 1000°C have a minimum at 40–60% of Al in the mixture [289]. It should be noted that the nature of the curve only changes significantly in the zone of a preferred siliciding and remains unchanged for mixtures rich in aluminum. Considerable increase in the thickness of diffusion layers obtained in mixtures rich in silicon, at 1000°C, is attributed by the authors to the sintering of the formed silicides and their consolidation with the main part of the layer. Unfortunately, the authors have not discussed the types of carbides formed and, consequently, sintered. It can be assumed that with an increase in temperature up to 1000°C, there is a variation in the kinetics of interaction between the impregnating medium and the substrate surface. The transition from diffusion kinetics to predominantly chemical kinetics, probably leads to the formation of porous silicide layers on the surface of an alloy.

Zemskov et al. [50] have also investigated the diffusion saturation of ZhS6K alloy with aluminum and silicon from a fine-disperse aluminum and silicon powder applied on the surface of a specimen with a binder. Uniform diffusion coatings were obtained after annealing in an inert (argon) atmosphere at temperatures above 850°C. Simultaneous surface impregnation of the alloy with silicon and aluminum was carried out at temperatures above 950°C. As in the case of impregnation in powders, with a rise in the silicon content of the active mixture, the thickness of aluminosiliconized layers increases on annealing at 1000°C whereas there is a decrease in thickness at much lower temperatures. It is recommended that aluminosiliconizing be carried out an ZhS6K alloy at 950–1050°C after covering it with a paste containing not more than 40 to 50% of silicon.

Results of investigations on aluminosiliconizing of nickel and its alloys in a gaseous medium by a circulation method are reported in [312]. For production of aluminosiliconized diffusion coatings, the author has recommended the following: the ratio of initial surface concentrations of nominal impregnating elements $F_{Si}/F_{Al}=1$; gas-flow velocity 1.21 m/s; temperature of the zone of formation of subchlorides of aluminum and silicon—1050°C; and temperature of the substrate metal—950°C.

Attempts of Nichiporenko and colleagues [307, 308] to obtain disilicide coatings alloyed with aluminum on the surface of tungsten, by simultaneous impregnation with aluminum and silicon, from a powder mixture in a vacuum, however, did not achieve positive results. By successive diffusion saturation with aluminum and silicon, diffusion layers containing tungsten disilicide alloyed with up to 10 at.% of aluminum were obtained.

The microhardness of aluminide, Fe_2Al_5, alloyed with silicon formed at the surface of iron and plain carbon steels, steel 45 and steel U8, aluminosiliconized by an aluminothermic process was found to be 755–665 kgf/mm^2. The microhardness of ordered solid solutions of FeAl and Fe_3Al, alloyed with silicon and of α-solid solution of aluminum and silicon in iron varies gradually with the thickness of the diffusion layer, from 450 to 190 kgf/mm^2.

Kidin et al. [298] have reported a gradual variation of microhardness along the thickness of an aluminosiliconized coating on steel 20 obtained by annealing paste-coated specimens, from 500 to 230 kgf/mm^2.

The wear resistance of aluminosiliconized coatings on steel R18 (hardness HRC 62) produced by an aluminothermic process, when tested for 2 h by dry sliding friction with a specific load of 10 kgf/mm^2 and a surface velocity of 1 m/s, was found to be 1.7 times less than the wear resistance of hardened and low-temperature tempered steel U8.

Multiphase coatings on steel produced in melts of aluminum and silicon, increase the ductility of the steel with a slight loss in strength [300].

Results of investigations on the heat resistance of aluminosiliconized as well as aluminized and siliconized specimens at 800, 900 and 1000°C are given in Table 26. With respect to resistance to oxidation at temperatures above 900°C, that of aluminosiliconized layers on Armco iron and steel U8 is better than that of siliconized layers which quickly disintegrate at 1000°C, whereas that of aluminized layers is slightly superior to the former. However, with a rise in the testing temperature the behavior of aluminosiliconized coatings with respect to heat-resistance is similar to that of aluminized coatings.

Results of studies on heat resistance of aluminized and aluminosiliconized coatings on alloy steels, at 1000°C are given in Table 27. Simultaneous diffusion impregnation with aluminum and silicon ensure better protection from high-temperature oxidation of 2Kh13 steel as compared to aluminizing. In the case of thinner diffusion coatings, aluminosiliconized layers on Kh18N9T and 3Kh19NMVT steels are less heat resistant than aluminized diffusion layer. Aluminizing or aluminosiliconizing of steel Kh25T, to improve its heat resistance, was found to be unsatisfactory. While aluminizing of steel 20Kh3MVF can protect it from high-temperature oxidation, aluminosiliconizing fails to prevent such oxidation.

Thus, it can be seen from the data given above that there is no evidence of a significant advantage of aluminosiliconizing of steel as compared to siliconizing and especially aluminizing. Only in some isolated cases does simultaneous diffusion coating with aluminum and silicon provide a much higher heat resistance to steel.

Aluminosiliconizing of ZhS6K alloy leads to improvement in the microhardness of the surface layers up to 800–900 kgf/mm^2 [289]. There is a slight reduction in microhardness when the aluminum content of the mixture is increased.

The heat-resistance of aluminosiliconized diffusion coatings on ZhS6K alloy, produced by a powder method in containers provided with fusible plugs and tested at 1100°C for 200 h, at any concentration of the active constituents of the impregnation mixture is higher than the heat-resistance of aluminized coatings on an alloy [289]. Silicon considerably increases the heat-resistance of the diffusion layer. The maximum heat resistance is that of a diffusion

Table 26

Coating	Impregnating medium	Material (substrate)	Temperature °C	Wt. gain, g/m^2 during testing period, h									
				6	16	26	36	46	56	66	76	86	100
Al	FeAl-base mixture	Armco iron	800	2.5	3.1	3.7	4.3	4.6	4.9	5.2	5.5	6.0	6.4
		U8		1.7	3.7	5.5	5.5	5.6	5.8	6.1	6.3	6.8	7.2
		Armco iron	900	5.2	5.9	6.3	6.8	7.5	7.7	8.2	8.5	8.9	9.4
		U8		4.1	6.2	8.1	10.1	13.0	13.4	13.9	14.6	15.8	16.7
		Armco iron	1000	5.7	10.9	13.8	16.8	22.5	24.8	26.3	28.7	29.8	31.6
		U8		9.6	14.5	18.0	21.8	26.1	29.5	34.7	37.1	39.9	43.5
Si	Eutectic KF+NaF base melt	Armco iron	800	0.8	1.5	1.8	2.4	3.0	3.7	4.5	4.5	4.8	5.5
		U8		0.3	1.0	1.6	2.8	2.9	3.0	3.5	3.9	4.4	5.2
		Armco iron	900	1.8	2.4	3.1	3.7	4.1	4.9	5.9	6.3	6.8	7.2
		U8		0.3	0.6	1.4	2.8	4.4	5.0	5.8	6.6	7.1	7.5
		Armco iron	1000	9.1	100	425	—	—	—	—	—	—	—
		U8		12.6	131	711			coating ineffective				
Al+Si	SiO_2+Al base mixture	Armco iron	800	6.5	10.1	10.1	13.3	13.5	14.7	16.0	16.9	17.6	19.8
		U8		8.4	10.0	11.3	14.1	16.1	17.8	19.2	21.6	22.0	24.2
		Armco iron	900	7.7	10.3	12.7	15.2	15.2	18.2	21.8	24.3	25.1	29.7
		U8		7.8	14.1	14.8	19.6	22.7	25.0	28.2	31.4	33.3	38.1
		Armco iron	1000	7.3	14.1	15.2	22.4	28.1	32.5	38.6	42.0	48.3	55.4
		U8		7.5	15.0	15.3	23.8	31.4	35.8	42.3	47.7	53.6	62.6

Table 27

Material (substrate)	Coating	Wt. gain, g/m² during testing period, h							
		6	26	46	66	86	100	120	150
20Kh3MVF	Without coating	710	1527	2330	3409	4393	4742	—	—
	Al	14.2	26.5	30.1	33.6	38.0	40.1	44.2	46.4
	Al+Si	90.8	137.2	560	1076	1542	1880	layer ineffective	
2Kh13	Without coating	324	496	782	1077	1363	1477	1959	2944
	Al	27.4	59.0	64.3	66.7	70.2	72.0	90.9	106.5
	Al+Si	8.8	25.6	29.9	32.5	36.9	38.0	44.0	49.3
Kh25T	Without coating	5.8	17.9	29.1	35.4	41.3	44.8	50.1	53.9
	Al	10.4	26.2	42.5	53.3	61.2	66.8	72.1	90.9
	Al+Si	21.6	23.7	48.5	57.6	62.6	66.8	70.3	74.8
Kh18N9T	Without coating	6.1	13.8	17.3	21.6	35.2	55.2	121.2	204.0
	Al	10.1	19.4	21.0	24.2	29.2	31.4	34.8	40.3
	Al+Si	15.7	23.1	26.0	30.7	35.8	38.1	43.5	52.5
3Kh19BMVBT	Without coating	34.4	—	—	—	—	—	—	2[illegible].0
	Al	10.0	21.6	31.3	40.6	54.3	64.2	74.1	84.2
	Al+Si	23.1	43.7	55.7	67.8	81.0	90.6	99.5	111.9

layer obtained by impregnation in a mixture containing 60% of Al and 40% of Si in an active mixture. The amount of active constituent in the mixture should be 50%. An increase in the temperature of impregnation from 900° to 1000°C improves the heat resistance of the diffusion layer. Further, it has been pointed out that aluminosiliconized layers have a higher resistance to diffusion desorption during testing at high temperatures.

During investigations on heat resistance it was observed that the concentrations of aluminum and silicon in diffusion layer decrease from 24 to 12% and 4 to 2%, respectively [289]. After testing for heat resistance, α-Al_2O_3 was found to be the predominant phase in aluminized and aluminosiliconized diffusion layers; silica was not found in the surface zone. The structure of an aluminosiliconized layer after testing also remained fine-disperse, and dark and retained a high microhardness. At grain boundaries, a fine network of Ni_3Al was observed. In aluminized layers, after testing, Ni_3Al phase forms a continuous zone near the surface.

The improved heat resistance of aluminosiliconized layers on nickel and its alloys, as compared to aluminized layers, has also been noted in [287, 312]. According to the data given in [312], an aluminosiliconized diffusion layer provides better protection to nickel-base alloys from oxidation at 1000–1200°C than does an aluminized layer.

Investigations on aluminosiliconized coatings by an aluminothermic process on ZhS6K nickel–chromium alloy have shown that they are in no way inferior to aluminized coatings which are used to improve the life of turbine blades for aerospace applications in regard to heat resistance, creep resistance, erosion resistance and fatigue strength are concerned.

4. VANADALUMINIZING

Simultaneous surface alloying of metals and alloys with vanadium and aluminum complexes improves their heat and corrosion resistance in a number of active mediums.

To date there is only one method of vanadaluminizing, viz. the aluminothermic treatment. Vanadium pentoxide is used as a source of active vanadium atoms and aluminum is used as a reducing agent. The effect of the ratio of vanadium pentoxide and aluminum in the charge and also of the quantity of the activator (AlF_3) in it on forming of vanadaluminized coating is shown in Fig. 2 (c).

At a 20% concentration of aluminum in the active mixture, a solid solution of vanadium in α-iron is formed on the surface of iron, whereas on the surface of steel U8 a carbide of vanadium, VC (4–7 μ) is formed, i.e. pure vanadium impregnation takes place. However, the presence of large quantity of free vanadium pentoxide in the mixture leads to pitting of the specimens and decarburization of the steel surface.

An increase in aluminum content beyond 20% is accompanied by a sharp rise in thickness of the diffusion layer on iron, as well as on steel, which indicates the simultaneous diffusion of vanadium and aluminum.

There are no traces of corrosion on the surfaces of the specimens in such cases. The maximum on the plot of thickness of the layer versus composition of the mixture, is observed at 30% of Al.

As the reduction of vanadium pentoxide by aluminum is a highly exothermic process, the amount of Al_2O_3, added as an inert substance in the active mixture is fairly large (60 wt.%).

A minimum on the plot of variation in thickness of the layer with the composition of the active mixture is observed at 35% of aluminum in the mixture. In the V–Al system, aluminides—VAl_3 and V_5Al_8—which are stable up to 1360 and 1670°C, respectively, are known to form [316]. X-ray diffraction analysis of the used mixture after aluminothermic reduction indicated complete absence of the aforementioned compounds. Consequently, they cannot be considered responsible for the reduction in thickness of the saturated diffusion layer. Thinning of the diffusion layer, as indicated above, can be attributed to a fall in potential of the diffusion source for every diffusing species and a concentration dependence of the coefficient of diffusion.

With a further increase in the aluminum content of the mixture, the thickness of the diffusion layer sharply increases owing to the impregnation of steel predominantly with aluminum (due to a rise in the potential of the diffusion source of aluminum and formation of a superlattice and, possibly, aluminides of iron). The optimum amount of activator, AlF_3, has been found to be 2–5%.

For optimizing the composition of the mixture for vanadaluminizing not only the rate of formation (Table 28) but the properties of the formed diffusion layers were also taken into account.

Results of investigations on the effect of the ratio between vanadium pentoxide and aluminum on the heat resistance of vanadaluminized steel 20 are given in Fig. 48. From this data, it can be seen that the highest heat resistance is that of a diffusion coating obtained by using a mixture containing V_2O_5 : Al = 40 : 60 wt.%.

The maximum corrosion resistance in dilute sulfuric acid is indicated by a coating of V_2O_5 : Al = 70 : 30 wt.%. From the data given above, the following parameters can be considered as optimum for obtaining coatings with the required properties:

1. For increasing the corrosion resistance of plain carbon steels (especially in sulfuric and phosphoric acids):

$$95\%\ [60\%\ Al_2O_3 + 40\%\ (60\text{–}70\%\ V_2O_5 + 40\text{–}30\%\ Al)] + 5\%\ AlF_3;$$

2. For improving their heat resistance:

$$95\%\ [60\%\ Al_2O_3 + 40\%\ (40\text{–}60\%\ V_2O_5 + 60\text{–}40\%\ Al)] + 5\%\ AlF_3.$$

Table 28

Composition of powder for vanadaluminizing, wt. %					Impregnating regime		Thickness of diffusion layer, μ			
[A Al_2O_3 + (100 − A) (x Al + y V_2O_5)] + n AlF_3 + m NH_4Cl							Material			
Al_2O_3	Al	V_2O_5	AlF_3	NH_4Cl	t, °C	τ, h	Commercial iron	Steel 20	Steel 45	Steel U8
60	20	80	5	0	1100	4		Pitting and decarburizing		
60	20	80	0	2	1100	4	70	—	—	4–7
60	30	70	5	0	1100	4		Pitting and decarburizing		
60	30	70	0	2	1100	4	175	—	140	125
								Coating nonuniform along the depth, decarburizing		
60	35	65	5	0	1100	4	140	—	120	100
60	40	60	5	0	1100	4	280	+	245	210
60	50	50	5	0	1100	4	380	−	315	295
40	40	60	5	0	1100	4	315	−	260	245
50	40	60	5	0	1100	4	280	−	250	210
60	40	60	5	0	1100	4	280	−	245	210
60	40	60	2	0	1100	4	280	−	210	210
60	40	60	5	0	1100	4	280	−	245	210
60	40	60	8	0	1100	4	210	−	190	155
60	40	60	5	0	900	2	70	70	65	55
60	40	60	5	0	900	4	120	105	90	85
60	40	60	5	0	900	8	140	120	105	90
60	40	60	5	0	1100	2	85	85	70	70
60	40	60	5	0	1100	4	160	155	140	140
60	40	60	5	0	1100	8	195	175	150	145
60	40	60	5	0	1100	2	210	210	175	165
60	40	60	5	0	1100	4	280	245	245	210
60	40	60	5	0	1100	8	330	315	280	245
60	50	50	5	0	1100	8	420	420	350	350
60	60	40	5	0	1100	8	595	525	455	420

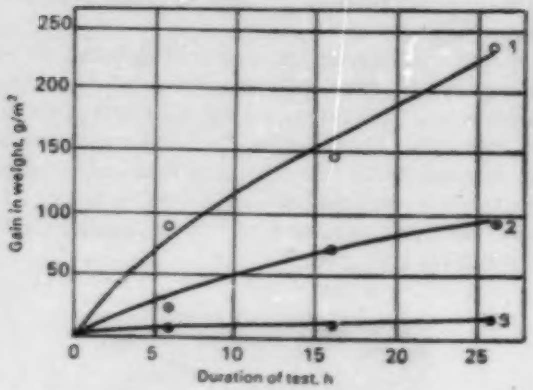

Fig. 48. Heat resistance of vanadaluminized steel at 100°C:
Ratio of V_2O_5 and Al in mixture: (1)—3 : 2; (2)—1 : 1; (3)—2 : 3.

The effect of temperature and duration of the treatment on thickness of the vanadaluminized diffusion coating on carbon steels using a mixture of the composition:

$$95\%\ [60\%\ Al_2O_3+40\%\ (50\%\ V_2O_5+50\%\ Al)]+5\%\ AlF_3,$$

is shown in Fig. 49.

Under optimum conditions of impregnation ($t=1000$–1100°C, $\tau=6$–8 h), diffusion layers with identical properties are formed on iron as well as on steel substrates: superlattice of FeAl and Fe_3Al alloyed with vanadium, transforming to a disordered solid solution of aluminum and vanadium in α-iron

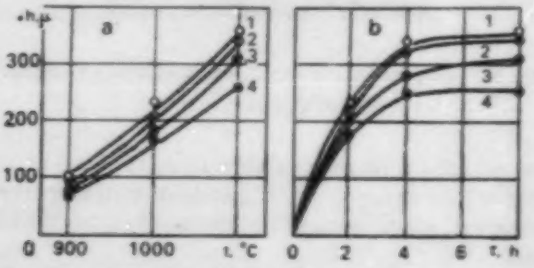

Fig. 49. Effect of temperature and duration of treatment on the thickness of vanadaluminized diffusion coatings on (1) iron, (2) steel 20, (3) steel 45, (4) steel U8:

Composition of the impregnating mixture: Al_2O_3—30%;
V_2O_5—60%; Al—40%; AlF_3—5%.

(a—$\tau=8$ h; b—$t=1100$°C).

(Fig. 50). An insignificant porosity has been reported in the surface zone of the FeAl phase.

The thickness of the diffusion layer, on iron and steel 20, steel 45 and steel U8, obtained by impregnation in mixtures with $V_2O_5 : Al = 40 : 60$ wt.% under the aforementioned conditions, is larger than that of coatings obtained from mixtures with $V_2O_5 : Al = 60 : 40$ wt.%. Further, the aluminum content in the coating obtained in the first mixture is found to be higher (it is well known that FeAl has a compositional range from 18 to 33% Al [313]). The microhardness of the diffusion layer gradually decreases from the surface to the volume, from 530 to 190 kgf/mm^2.

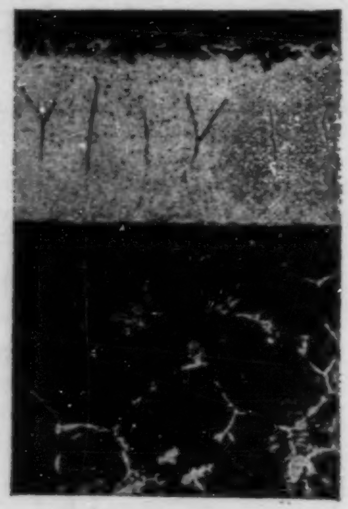

Fig. 50. Microstructure of vanadaluminized layer on steel 45: $t = 1000°C$, $\tau = 8$ h, ×200.

In the zone of α-phase (disordered solid solution of aluminum and vanadium in α-iron) on steel 45 and steel U8, precipitation of a ternary compound, Fe_3AlC_x, is observed, which segregates preferentially along the boundaries of acicular grains.

The concentration of aluminum on the surface of steel 45 reaches 33.1% (after impregnation for 8 h at 1100°C in a mixture with $V_2O_5 : Al = 40 : 60$ wt.%). The presence of vanadium in the diffusion layer was established by qualitative spectral analysis.

A quantitative analysis could not be conducted due to the nonavailability of standard specimens.

Vanadaluminized steels have a high heat resistance. The heat resistance of vanadaluminized steels, impregnated in a mixture with $V_2O_5 : Al = 40 : 60$ wt.% for 8 h at 1100°C, has been studied. Investigations on heat resistance were conducted at 1000°C for 26 h. The rate of oxidation was computed from the weight gain, corresponding to the initial surface area of the specimen. The results obtained are given in Table 29.

Table 29

Coating	Conditions of vanadaluminizing		Wt. gain, g/m² at 1000°C for 26 h testing			
	t, °C	τ, h	Commercial iron	Steel 20	Steel 45	Steel U8
Untreated metal	—	—	1454	1310	1395	1100
V–Al	1100	8	35.2	8.95	40.0	37.8

Depending on the type of steel, the heat resistance of diffusion impregnated specimens is found to improve by 30 to 145 times as compared to that of untreated base metal.

Vanadaluminized steels have a better heat resistance than similar aluminized steels (Table 30).

Table 30

Coating	Relative heat resistance at 1000°C, 26 h		
	Steel E12	Steel 45	Steel U8
V–Al	32	38	8
Al (from powder)	3	9	15
Al (aluminothermic)	6	3	2
Al (liquid)	6	3	—

Vanadaluminizing significantly improves corrosion resistance (Table 31).

The corrosion resistance of vanadaluminized plain carbon steels in the acids used in investigations was found to be 2–3 times higher than that of untreated material.

5. TITANOALUMINIZING

Simultaneous diffusion saturation of surface layers of steels with titanium and aluminum improves their heat and corrosion resistance in various corrosive mediums. However, in many cases, a much better heat-resistant coating can be obtained by aluminizing alone.

Table 31

Testing medium	Wt. loss, g/m² for 75 h testing							
	Untreated metal				After vanadaluminizing			
	Commercial iron	Steel 20	Steel 45	Steel U8	Commercial iron	Steel 20	Steel 45	Steel U8
3% NaCl	11.6	5.2	4.5	87	2.0	3.9	5.0	1.2
10% H_2SO_4	32.0	76.0	832.0	1200.0	67.0	36.0	495.0	50.0
30% HCl	592.0	1766.0	3543.0	1389.0	447.0	1198.0	1315.0	1298.0
40% H_3PO_4	43.0	113.0	1192.0	1173.0	26.0	138.0	130.0	25.0
10% HNO_3	6128	5748	6070	5720	484	2573	2491	1788
50% CH_3COOH	42.0	39.0	44.0	42.0	30.0	32.0	32.0	22.0

Generally for titanoaluminizing, powders of either titanium and aluminum or their ferroalloys are used [1, 20, 24, 313, 314 and others]. Titanoaluminizing in ferrotitanium- and ferroaluminum-base pastes have also been investigated [298]. The use of metal baths which, in addition to aluminum and silicon, also contain calcium, barium and strontium (or one of these metals), have also been proposed for titanoaluminizing [311].

The dependence of the thickness of diffusion layers on the ratio of aluminum and titanium in powder mixtures, for Armco iron and steel 45 is shown in Fig. 51 (a and b). In powder mixtures of diffusing elements, with and without activator additions, a reduction in the thickness of the diffusion layer is observed with an increasing concentration of titanium in the mixture. This can be attributed to a decrease in the concentration of the fast-diffusing element, i.e. aluminum in the mixture. Gradual substitution of one diffusing species by another leads to a variation in the composition of stable ferrite (in mixtures without an ammonium-chloride additive). With an activator in the

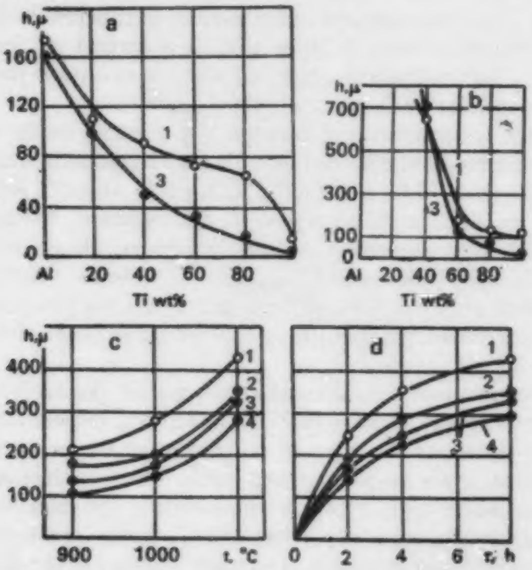

Fig. 51. Effect of composition of powder mixture and diffusion coating on regime on the depth of titanoaluminized diffusion layers on:

(1) Armco iron, (2) Steel 20, (3) Steel 45 and (4) Steel U8: a—Mixture without activator ($t=1000°C$, $\tau=6$ h); b—Mixture with activator (same impregnation regime); c—Mixture: 30% Al_2O_3 + 50% TiO_2 + 50% Al + 5% AlF_3 + 2% ammonium chloride, $\tau=8$ h; d—Same mixture composition as (c), $t=1100°C$.

mixture, along with α-solid solution of titanium and aluminum in iron, an aluminide layer is also formed. Further investigations are necessary in order to establish the presence of compounds (such as aluminide of titanium) in the surface layer. However, even if these compounds do form in the mixture, the activity of the mixture is significantly altered.

Titanoaluminized coatings on different metals and alloys can also be obtained by using a powder mixture of aluminum and titanium oxide, containing an amount of aluminum in excess of that required for complete reduction of TiO_2.

At up to a 30% aluminum content in the mixture, a titanized coating is formed on the surface of iron and steels. The diffusion layer on Armco iron consists of two zones—the titanide, Fe_2Ti and acicular α-solid solution of titanium in iron. The coating on carbon steels consists of titanium carbide, TiC. On increasing the aluminum content in the mixture up to 30%, the thickness of the titanized layer on iron gradually increases, but, practically no change is observed in the coating on steel U8.

When the aluminum contents in the mixture is between 30–50%, a two-component titanoaluminized diffusion coating is formed on the surface of iron and steels, the thickness of which, on plain carbon steels increases with an increase in the aluminum content in the mixture.

The effect of temperature and duration of processing on the thickness of the titanoaluminized layer obtained by diffusion saturation in a mixture consisting of: $100\% \, [30\% \, Al_2O_3 + 70\% \, (50\% \, TiO_2 + 50\% \, Al)] + 5\% \, AlF_3$, is shown in Fig. 51 (c and d). The diffusion layer on the surface of Armco iron, steel 45 and steel U8 comprises a zone of aluminide, Fe_2Al_5, alloyed with titanium, with finely-dispersed inclusions of aluminide, TiAl, below which is located a zone of ordered solid solutions of FeAl and Fe_3Al, alloyed with titanium, with finely-dispersed inclusions of Ti_3Al and α-solid solution of titanium and aluminum in iron.

The concentration of titanium and aluminum on the surface of titanoaluminized steel 45 was found to be 28.9% and 37.3%, respectively.

Figure 52 represents the effect of alloying elements on the thickness of titanoaluminized layers on plain carbon steels. The introduction of silicon, chromium and nickel up to 3% favor an increase in the thickness of titanoaluminized layers. An especially strong effect, among the alloying elements investigated, is provided by silicon. The microstructure of the diffusion layer on medium carbon steel is shown in Fig. 53.

Variations in the conditions of treatment (ratio of TiO_2/Al in the powder mixture, temperature and other parameters) can bring about changes in the dependence of the thickness of a titanoaluminized coating on the concentration of alloying elements in the steel, thereby significantly modifying the structure and chemical composition of the diffusion layer as well as its properties.

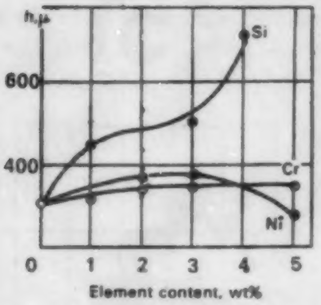

Fig. 52. Effect of alloying elements on the thickness of titanoaluminized layers on medium carbon steel (0.4% C):

$t = 1100°$ C, $\tau = 8$ h.

The effectiveness of alloying elements in influencing the thickness of a titanoaluminized layer on medium carbon steel can be estimated from Fig. 52. A significant influence of alloying elements on heat resistance could also be expected. However, it has been established that silicon and chromium (up to 4 and 5%, respectively) do not have any noticeable influence on heat resistance (Fig. 54). At the same time, alloying with these elements (especially silicon) helps in producing thicker diffusion layers thereby improving the durability of the coating. Alloying of medium carbon steels with nickel results in a reduction in its thermal stability.

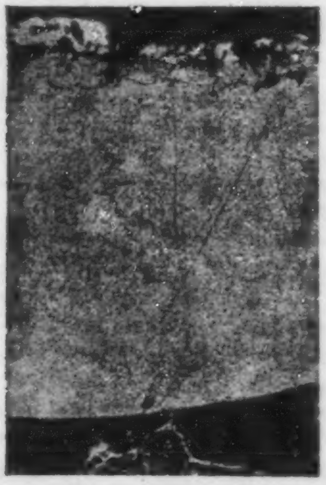

Fig. 53. Microstructure of titanoaluminized steel 45 (×200).

Optimizing the production of heat-resistant coatings by titanoaluminizing, employing statistical modeling of experiments, led to a precise determination of the treatment parameters (given below), ensuring a maximum heat resistance of Armco iron and steel U8.

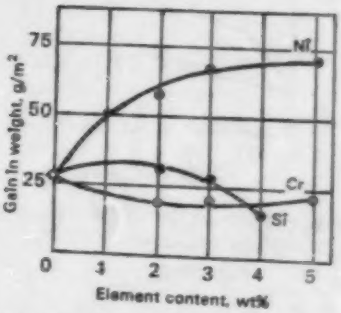

Fig. 54. Effect of alloying elements on heat resistance of titanoaluminized medium carbon steel (0.4% C):

Testing parameters: $t = 1000$°C, $\tau = 26$ h.

Mixture composition, wt.%:

100% [35% Al_2O_3 + 65% (45% TiO_2 + 55% Al)] + 4% AlF_3;

Treatment temperature: 1050–1080°C, duration 6–7 h.

The concentration of titanium and aluminum in surface layer of titanoaluminized steel U8, under the conditions indicated above, was found to be 17.4% and 27.5%, respectively.

Investigations on the heat resistance of titanoaluminized layers indicate that diffusion saturation of iron and plain carbon steels simultaneously with titanium and aluminum for improving their resistance to oxidation at high temperatures (Table 32) does offer any advantage over pure aluminizing. Titanoaluminized layers were found to be thinner and oxidized much faster than aluminized layers.

Results of investigations on heat resistance of aluminized and titanoaluminized diffusion coatings at 1000°C on some alloy steels are shown in Table 33. On all the steels except steel 2Kh13, aluminized diffusion coatings exhibit good heat resistance. At the same time it should be noted that in all the steels investigated the thickness of the titanoaluminized layer was 1.5–2 times more than that of aluminized layers. It can, therefore, be expected that during prolonged testing, a titanoaluminized layer will indicate a better heat resistance than an aluminized layer.

A titanoaluminized layer on steel U8 obtained in aluminothermic mixtures, exhibits two times more wear resistance (under conditions of dry

Table 32

Base material	Testing tempera-ture, °C	Wt. gain for titanoaluminized specimens, g/m² for duration of test, h									
		6	16	26	36	46	56	66	76	86	100
Armco iron	800	1.6	2.5	2.9	3.2	4.1	5.2	5.3	6.4	6.7	7.3
	900	3.3	6.7	9.1	12.3	12.4	13.4	13.6	15.8	16.0	16.2
	1000	8.9	14.0	14.0	17.2	20.1	21.7	23.1	26.4	27.2	28.5
Steel U8	800	1.8	4.2	5.1	5.1	6.0	7.4	7.6	8.2	9.3	10.2
	900	3.4	9.7	12.3	14.1	16.9	17.0	20.8	21.3	23.4	25.0
	1000	6.9	17.9	17.9	23.1	28.2	34.1	37.3	43.6	46.0	51.8

Table 33

Base material	Diffusion layer	Wt. gain, g/m², during testing, for h							
		6	26	46	66	86	100	120	150
20Kh3MVF	1	710	1527	2330	3409	4393	4742	—	—
	2	14.2	26.5	30.1	33.6	38.0	40.1	44.2	46.4
	3	7.2	17.1	23.0	28.8	37.9	48.4	58.3	76.2
2Kh13	1	325	497	782	1078	1364	1478	1959	2944
	2	27.4	59.0	64.3	66.7	70.2	72.0	90.0	106.5
	3	2.2	8.2	14.4	18.7	25.1	29.1	38.9	48.4
Kh25T	1	5.8	17.9	29.1	35.4	41.3	44.8	50.1	53.9
	2	10.4	26.2	42.5	53.3	61.2	66.8	72.1	90.9
	3	6.1	20.8	41.0	55.1	68.2	78.5	93.0	101.1
Kh18N9T	1	6.1	13.8	17.3	21.6	35.2	55.2	121.2	204.0
	2	10.1	19.4	21.0	24.2	29.2	31.4	34.8	40.3
	3	3.2	20.5	35.5	47.0	56.4	63.0	71.0	83.2
3Kh19N9MVBT	1	34.4	—	—	—	—	—	—	280.0
	2	10.0	21.6	31.3	40.6	54.3	64.2	74.1	84.2
	3	5.5	13.6	28.9	49.3	75.5	83.8	89.7	101.4

Note: Testing temperature 1000°C, 1—Without coating; 2—Titanoaluminized; 3—Aluminized.

sliding friction) than hardened and low-temperature tempered steel U8. Further, a titanoaluminized coating has a higher corrosion resistance in a solution of NaCl and dilute nitric and acetic acids.

Zemskov et al. [1, 20, 24, 313, 314 and others] have investigated titanoaluminizing of ZhS6K nickel alloy in a powder mixture of elements. Surface alloying was carried out at 850°C and 1000°C in containers with fusible lids. Ammonium chloride was used as an activator. Simultaneous surface alloying of ZhS6K alloy with titanium and aluminum takes place when the titanium content in the mixture is in the range of 35–95%. At titanium concentrations below 35% a preferred aluminizing takes place, whereas a preferential diffusion impregnation of titanium occurs at titanium concentrations of above 95%. The thickness of the diffusion layer gradually decreases with increasing titanium content in the active mixture. The authors recommend the following regime for titanoaluminizing: 900°C, duration of impregnation in a powder mixture containing 60–80% of titanium: 10–15 h. $TiAl_3$ and Ni_3Al-base phases have been observed in the surface layer on ZhS6K alloy.

A powder mixture consisting of 50–70% of titanium, 20–48% of aluminum and 0.5–9% of combined carbon has been proposed for diffusion coating of nickel-base heat-resistant alloys [314].

While short duration tests on titanoaluminized coatings on ZhS6K (impregnation in aluminothermic mixtures) indicate that they are more heat resistant than aluminized coatings, contrary results were obtained when the duration of tests was significantly long (150 h).

Treatment of nickel–chromium alloys in powder mixtures containing 15% titanium and 6% of aluminum in an inert atmosphere, improves the resistance to intergranular corrosion and increases the thermal-shock resistance [315].

The data given here indicates that present investigation on titanoaluminizing of metals and alloys and the properties of such coatings produced by diffusion saturation are not suitable for use. High-temperature oxidation resistance and corrosion resistance in different corrosive mediums along with improved wear resistance are important features of steels simultaneously impregnated with titanium and aluminum. Possibly, titanoaluminized steels can find application in oxidizing atmosphere in friction coupling.

6. ZIRCOALUMINIZING

Simultaneous impregnation of metals and alloys with zirconium and aluminum improves their heat and corrosion resistance in a number of corrosive mediums.

Surface alloying can be carried out either in powders of elements, according to the technology reported in [1, 20, 288, 303] or in powdered oxides by an aluminothermic method [102].

The effect of the composition of the mixture on the thickness of the diffusion layer is shown in Table 34.

Table 34

Mixture composition wt.% 100% [A Al_2O_3+(100−A) (x Al+y ZrO_2)]+n AlF_3				Parameters of zirco-aluminizing		Total thickness of layer, μ			
Al_2O_3	Al	ZrO_2	AlF_3	t°, C	τ, h	Armco iron	Steel 20	Steel 45	Steel U8
30	10	90	5	1100	4	55	50	40	35
30	20	80	5	1100	4	90	80	75	70
30	25	75	5	1100	4	105	105	100	75
30	30	70	5	1100	4	125	125	90	85
30	40	60	5	1100	4	155	155	125	120
30	50	50	5	1100	4	325	325	315	295
20	50	50	5	1100	4	350	325	315	315
30	50	50	5	1100	4	335	325	315	295
40	50	50	5	1100	4	315	300	280	280
30	50	50	2	1100	4	210	210	195	160
30	50	50	5	1100	4	335	325	315	295
30	50	50	8	1100	4	210	190	175	140
30	50	50	5	900	2	140	125	105	85
30	50	50	5	900	4	160	140	120	90
30	50	50	5	900	8	210	175	160	140
30	50	50	5	1000	2	160	140	125	105
30	50	50	5	1000	4	190	175	160	155
30	50	50	5	1000	8	245	230	210	195
30	50	50	5	1100	2	280	270	260	250
30	50	50	5	1100	4	335	325	315	295
30	50	50	5	1100	8	370	350	335	315

A slight difference in the thickness of the diffusion layer on iron and plain carbon steels in the whole range of compositions of active mixtures indicates a predominance of aluminum in the diffusion layer.

The thickness of the diffusion coating increases with an increase in the aluminum content of the impregnating mixture. This rise in thickness is very sharp at aluminum contents of 40% and above.

The optimum concentration of an activator (AlF_3) has been found to be 5%.

Zirconia manifests a low reducibility with aluminum. During thermochemical treatment, the degree of reducibility of zirconium dioxide rises due to the formation of a gaseous compound of zirconium which transports zirconium away from the reaction zone and also due to its diffusion in the metal substrate. Thus, the equilibrium of reaction

$$3ZrO_2 + 4Al = 2Al_2O_3 + 3Zr$$

shifts in the right-hand direction.

On the basis of metallographic, spectroscopic and x-ray analysis of diffusion layers, the following composition of the impregnating mixture was found optimum for zircoaluminizing:

$$95\% \, [30\% \, Al_2O_3 + 70\% \, (50\text{–}60\% \, ZrO_2 + 50\text{–}40\% \, Al)] + 5\% \, AlF_3.$$

Typical microstructures of the surface coatings on iron and plain carbon steels, obtained by treatment in a mixture of the composition given above are shown in Fig. 55.

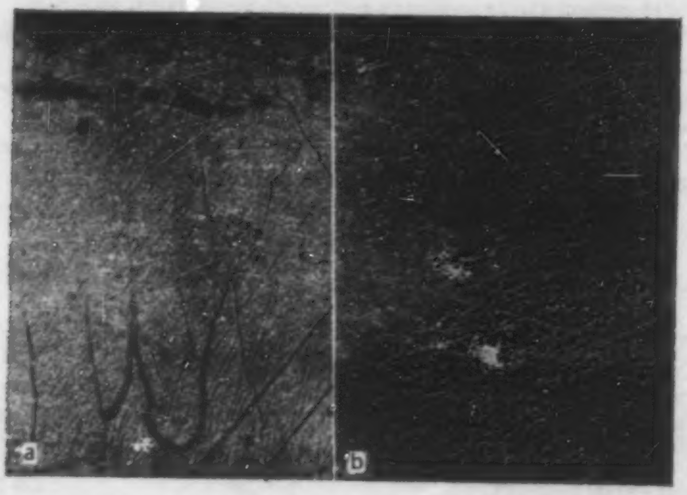

Fig. 55. Microstructure of zircoaluminized layers on (a) Armco iron and (b) steel 45.

The effect of temperature and the duration of the treatment on the thickness of a diffusion layer is shown in Fig. 56.

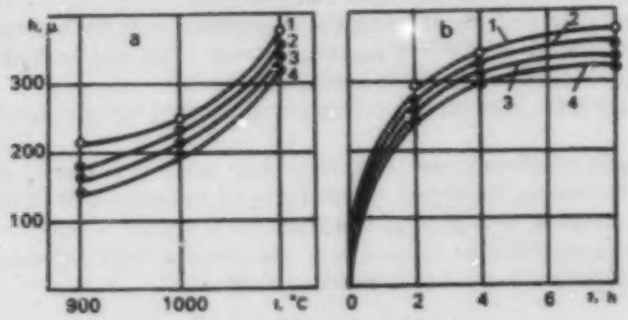

Fig. 56. Kinetics of zircoaluminizing in an aluminothermic mixture—
30% Al_2O_3 + 70% [(50% + ZrO_2 + 50% Al)] + 5% AlF_3:
1—Armco iron; 2—steel 20; 3—steel 45; 4—steel U8
(a—$\tau = 8$ h; b—$t = 1100$°C).

X-ray structural analysis has established the formation of zirconium aluminide, $ZrAl_2$ on the surface of iron and carbon steels. Aluminide of iron, Fe_2Al_5, alloyed with zirconium exists beneath the $ZrAl_2$ layer.

Below this are situated the zone of solid solution consisting of a superlattice of FeAl and Fe_3Al alloyed with zirconium and a disordered solid solution of aluminum and zirconium in α-iron with an columnar structure.

The aluminum concentration on the surface of carbon steels ranges between 45–65%.

In the zone of solid solutions formed on steel, a preferred precipitation of Fe_3AlC_x, of columnar grains takes place at the boundaries.

The microhardness of individual zones of the diffusion layer, to a certain content, depends on the carbon concentration (Table 35).

Table 35

Phase in zircoaluminized layer	Microhardness, kgf/mm^2	
	Commercial iron	Steel 45
$ZrAl_2$	945–840	945–890
Fe_2Al_5	795–675	795–715
Zone of solid solution (FeAl + Fe_3Al + α-phase)	515–210	520–230

Zircoaluminized carbon steels have an improved heat resistance (Table 36), which is, however, much lower than that of aluminized steels.

Table 36

Coating	Wt. gain, g/m² at 1000°C, 26 h			
	Commercial iron	Steel 20	Steel 45	Steel U8
Untreated metal	1454	1310	1395	1100
Zircoaluminized	96.5	110	170	186
Aluminized	18	32	17	31

On the ZhS6K nickel alloy, the improvement in heat resistance by zircoaluminizing is more than that obtained by pure aluminizing [288] (Fig. 57).

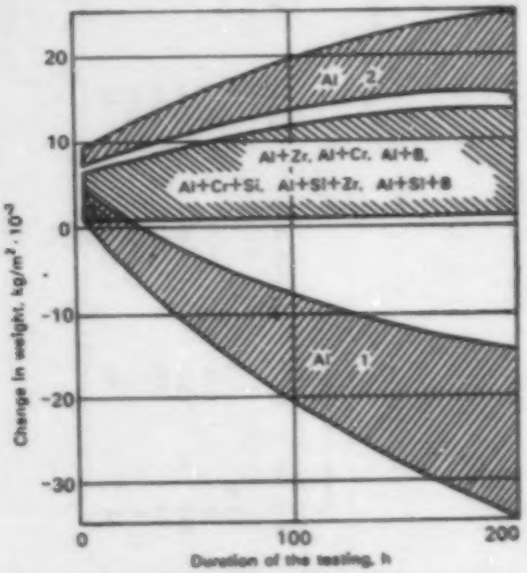

Fig. 57. Comparative oxidizability of ZhS6K alloy after diffusion coating (using different types of impregnation).

Zircoaluminizing does not protect carbon steels from corrosion in dilute acids (Table 37). However, a slight improvement in corrosion resistance

Table 37

Composition of the medium	Wt. loss, g/m^2 during 75-h test							
	Commercial iron		Steel 20		Steel 45		Steel U8	
	Untreated	Zr–Al	Untreated	Zr–Al	Untreated	Zr–Al	Untreated	Zr–Al
3% NaCl	11.6	2	5.2	2	4.5	8	8.7	9
10% H_2SO_4	32	1639	76	1494	832	1997	1200	1724
30% HCl	592	1579	1766	2292	3543	2021	1389	2430
40% H_3PO_4	43	1378	113	1694	1192	1761	1173	2992
10% HNO_3	6128	55	5748	5275	6070	2201	5720	510
50% CH_3COOH	42	43	39	54	44	214	42	99

resulting from zircoaluminizing of low-carbon steels in sea water has been noticed.

There is no data in the literature on any other properties of zircoaluminized coatings on metals and alloys.

CHAPTER II

Two-component Coatings Containing Boron

1. BOROSILICONIZING

Borosiliconizing is employed for improving wear resistance and sometimes, for increasing corrosion and heat resistance.

Simultaneous diffusion impregnation with boron and silicon can be carried out in powder mixtures [26, 271, 317], as well as in fused baths using electrolytic [77, 318] or electroless techniques [319]. Diffusion saturation of iron and steel with boron and silicon in pulverized mixtures has been investigated [26, 271, 317]. For surface impregnation a powder mixture consisting of boron carbide, crystalline silicon (or ferrosilicon) and ammonium chloride [(84% B_4C + 16% $Na_2B_4O_7$) + (95% Si + 5% NH_4Cl)] has been successfully used. In future (for the sake of simplicity) constituent No. 1 (84% B_4C + 16% $Na_2B_4O_7$) will be referred to as the boron-bearing component and constituent No. 2 (95% Si + 5% NH_4Cl)—as the silicon-bearing component. A pulverized mixture of specified composition was charged along with the specimens in a container provided with fusible lids and held for a predetermined period in a tubular furnace at the specified temperature. Results of diffusion coating were evaluated by means of data from metallographic, phase, x-ray and microprobe analyses. The effects of the composition of the active mixture, temperature and duration of the treatment on the thickness and structure of diffusion layers have been investigated in the aforementioned works.

Table 38

Composition of borosiliconizing mixture at temperature 1000°C, 6 h	Phases in the resultant coating
95% (84% B_4C + 16% $Na_2B_4O_7$) + 5% (95% Si + 5% NH_4Cl)	FeB, Fe_2B
90% (84% B_4O + 16% $Na_2B_4O_7$) + 10% (95% Si + 5% NH_4Cl)	Fe_2B, FeB, FeSi
80% (84% B_4C + 16% $Na_2B_4O_7$) + 20% (95% Si + 5% NH_4Cl)	Fe_2B, FeSi
75% (84% B_4C + 16% $Na_2B_4O_7$) + 25% (95% Si + 5% NH_4Cl)	FeSi, Fe_2B

It has been established that the results of diffusion coating are strongly influenced by the composition of the impregnating mixture (Table 38) [271]. On borosiliconizing using powder mixtures containing less than 10% of component No. 2 (by weight), the diffusion coating consists of borides of iron FeB and Fe_2B (apparently alloyed with silicon) and solid solutions of boron and silicon in iron. On increasing the concentration of component No. 2 in the active mixture beyond 10%, silicides of iron are formed in the diffusion layer. The rise in silicon content of the impregnating mixture is accompanied by a corresponding reduction in the content of high-boron phase (FeB) in the diffusion layer and at concentrations of component No. 2 in the mixture of 20% or more the boride, FeB, does not form in the diffusion layer. On impregnation of steel in active mixtures containing less than 20% of component No. 2, the resultant coating consists only of silicides of iron. The thickness of the diffusion layer decreases with an increase in the silicon content of the impregnating mixture (Table 39) [271].

Table 39

Composition of mixture		Thickness of borosiliconized coating, μ t—1050°C, τ—4 h		
84% B_4C + 16% $Na_2B_4O_7$	95% Si + 5% NH_4Cl	Commercial iron	Steel 45	Steel U8
95	5	365	343	328
85	15	354	332	319
75	25	326	310	290
65	35	300	276	263
50	50	265	242	227
45	55	250	226	205
40	60	236	217	192
30	70	195	180	175
25	75	191	174	151

In [271] Kaidash has shown that the temperature and time dependence of the growth of the diffusion layer are of an exponential and parabolic nature, respectively. However, in our view, this is not a correct conclusion, as variation in the impregnation parameters would lead to an alteration in the correlation between the boride and silicide phases in the diffusion layer, and this will consequently lead to a violation of the aforesaid nature of dependence.

The kinetics of formation and growth of a borosiliconized layer on iron can be represented as follows: The formation of a solid solution of boron and silicon in iron (α-phase) takes place at the beginning of impregnation. As the rate of diffusion of boron in α-phase is higher than the rate of diffusion of silicon, boron accumulates at the interface between the diffusion layer and the metal substrate. This results in the formation of a boride phase. When the treatment is carried out for a fairly long period, the boride phase at the diffusion layer—substrate metal interface forms a continuous layer which effectively prevents penetration of silicon into the metal. The concentration of silicon in the diffusion layer builds up at a fairly fast rate. This is also assisted by the process of formation of a boride phase at the surface of the steel being treated. The solubility of silicon in borides is not high and, during formation of boride phases, it is squeezed into the adjoining part of the layer. The processes indicated may consequently lead to the formation of silicides of iron. According to Kaidash [271], the silicon content in a borosiliconized coating reaches 8.3%.

Redistribution of carbon is observed during borosiliconizing of steels. From the diffusion saturated layer, carbon moves into the volume of the metal.

A zone rich in carbon is formed beneath the coating. Displacement of carbon from the diffusion layer is due to the formation of those phases in which carbon is practically insoluble. In all the regimes of impregnation and compositions of the reaction mixture, carbon was found to be responsible for a reduction in thickness of the diffusion coating.

Electrolytic borosiliconizing was first reported by Blun et al. [318]. Melts for borosiliconizing were prepared by fusing boric anhydride (B_2O_3), quartz sand (SiO_2) and soda ($NaCO_3$) in such proportions that the ratio (B_2O_3+SiO_2)/Na_2O remained constant during all the experiments and only the ratio B_2O_3/SiO_2 was varied. Sodium fluoride was introduced in the melt to improve its fluidity. At an impregnation temperature of 1040°C, for a cathode current density of 0.7 A/cm^2 a process duration of 30 min., in melts with $B/Si > 0.86$, only boriding took place. The borided layer had a typical acicular structure and consisted of borides, FeB and Fe_2B. Simultaneous diffusion saturation of steel with boron and silicon occurred at a ratio of boron and silicon in the melts of between 0.5 to 0.86. In addition to boride phases, silicides of iron (FeSi, $FeSi_2$) were also present in the diffusion layer. Finally, only siliconizing occurred at B/Si ratios in the melt below 0.4% (silicides, FeSi and $FeSi_2$, have been detected in the diffusion layer). According to the authors of [318], the direction of the reaction at the cathode was determined by the 'activity' of boron and silicon, which in turn depends on the ratio of B/Si deposited at the cathode (the latter is probably determined by the ratio B/Si in the bath) and also by the atomic radii of boron and silicon.

In our investigations, melts of the $Na_2B_4O_7$–Na_2SiO_3 system were used for electrolytic borosiliconizing. Melts were prepared by fusing borax and sodium monosilicate which, in turn, was obtained by fusing quartz sand (SiO_2) with soda. Analytical grade borax was dehydrated and prefused in silica crucibles in an electrically heated shaft furnace using Silit heating elements. Specimens were introduced in the electrical circuit as cathode. A graphite rod served as the anode. Power connections to the graphite rod and specimens were made using threaded joints. The location of electrodes (distance between electrodes from the bottom of the crucible) was maintained constant by using special gadgets and accessories. In order to study the phases formed at different compositions of the impregnation mixture and voltage, in the structure of the layer, borosiliconizing was carried out at 1050°C, using the following compositions of the mixture:

100% $Na_2B_4O_7$,
90% $Na_2B_4O_7$ + 10% Na_2SiO_3,
80% $Na_2B_4O_7$ + 20% Na_2SiO_3,
70% $Na_2B_4O_7$ + 30% Na_2SiO_3,
60% $Na_2B_4O_7$ + 40% Na_2SiO_3,
50% $Na_2B_4O_7$ + 50% Na_2SiO_3,
40% $Na_2B_4O_7$ + 60% Na_2SiO_3,
30% $Na_2B_4O_7$ + 70% Na_2SiO_3,
20% $Na_2B_4O_7$ + 80% Na_2SiO_3,
10% $Na_2B_4O_7$ + 90% Na_2SiO_3,
5% $Na_2B_4O_7$ + 95% Na_2SiO_3,
100% Na_2SiO_3.

Electrolytic surface impregnation was carried out at different voltages between 0.5 to 5 V. The duration of every experiment was kept constant at 30 min. The results of metallographic analysis of diffusion saturated boro-aluminized specimens are given in the form of a plot of phases formed at different compositions of the melt versus voltage (see Fig. 18).

The deposition potentials of boron (using pure borax) and silicon (using pure sodium monosilicate) were determined from the point of intersection of the abscissas with the extrapolated linear parts of the plot of thickness of the diffusion layer versus voltage. In electrolysis of a melt of a borax-sodium silicate system, the deposition voltage for boron was measured according to the formation of boride phase on the surface of the steel specimen and the deposition voltage for silicon was fixed according to the formation of a solid solution of silicon in iron.

As can be seen from Fig. 18, during electrolysis of melts containing up to 40 wt.% of Na_2SiO_3, a boride diffusion coating is formed on the steel cathode. In the case of melts containing more than 40 wt.% of Na_2SiO_3, three types of diffusion coatings may be formed: siliconized (α-solid solution of silicon in iron), borosiliconized (α-solid solution of silicon in iron and boride phases) and a layer of borides.

In melts containing less than 40% of sodium monosilicate it was found impossible to determine the deposition potential for silicon by metallographic analysis. This can be explained by the fact that the atoms of silicon deposited at the cathode, do not form an independent phase with iron due to their very low concentration on the specimen surface and are, therefore, alloyed with borides of iron. The feasibility of alloying silicon with borides has also been indicated by Blanter and Besedin, and Zemskov and Kaidash [320, 26].

Possibly, borides in borosiliconized coatings are also alloyed with silicon.

In spite of only a moderate accuracy of determination of the deposition potentials of boron and silicon, the plots of the phase formed at different compositions of the melt and voltages, based on experimental data on the constituent phases, offer a visual representation of the mechanism of electrolytic borosiliconizing, which fully confirms the mechanism of borosiliconizing of the electrolytic method, proposed earlier by the authors.

Electroless liquid-phase diffusion saturation of steel with boron and silicon is based on the principle of carbide reduction of the corresponding oxides.

The existence of two carbide agents, very similar to each other in their interatomic bonding and physicochemical properties—boron carbide and carborundum—reveals a possibility of 'cross' carbide reduction, during which one impregnating element enters the metal due to the reduction of oxide by the carbide and the other—due to thermochemical decomposition of the carbide at the surface of the metal being impregnated. Thus, a borosiliconized layer can be obtained in two ways:

1) by the reduction of sodium monosilicate by boron carbide (B_4C);
2) by the reduction of $Na_2SiO_3 + Na_2B_4O_7$ by silicon carbide (SiC).

In the first case active atoms of silicon are formed during chemical reduction of silica by boron carbide, which is also the diffusion source of boron.

In the second case, active atoms of boron are the result of a reduction of borax by carborundum. SiC acts as the diffusion source of silicon.

The ratio of active atoms of boron and silicon, formed during the chemical reaction can be varied by altering the quantitative ratio between the constituents of the impregnating mixture, thereby influencing the structure, constituent phases, composition and characteristics of the resultant diffusion layers.

In our investigations, experiments were carried out using melts of the following compositions:

1) 75% $Na_2SiO_3 + 35\%\ (SiC + B_4C)$;
2) 75% $(Na_2B_4O_7 + Na_2SiO_3) + 35\%$ SiC.

In the first case silicon carbide was gradually substituted by boron carbide iron), borosiliconized (α-solid solution of silicon in iron and boride phases) and a layer of borides.

In melts containing less than 40% of sodium monosilicate it was found impossible to determine the deposition potential for silicon by metallographic analysis. This can be explained by the fact that the atoms of silicon deposited at the cathode, do not form an independent phase with iron due to their very low concentration on the specimen surface and are, therefore, alloyed with borides of iron. The feasibility of alloying silicon with borides has also been indicated by Blanter and Besedin, and Zemskov and Kaidash [320, 26].

Possibly, borides in borosiliconized coatings are also alloyed with silicon.

In spite of only a moderate accuracy of determination of the deposition potentials of boron and silicon, the plots of the phase formed at different compositions of the melt and voltages, based on experimental data on the constituent phases, offer a visual representation of the mechanism of electrolytic borosiliconizing, which fully confirms the mechanism of borosiliconizing of the electrolytic method, proposed earlier by the authors.

Electroless liquid-phase diffusion saturation of steel with boron and silicon is based on the principle of carbide reduction of the corresponding oxides.

The existence of two carbide agents, very similar to each other in their interatomic bonding and physicochemical properties—boron carbide and carborundum—reveals a possibility of 'cross' carbide reduction, during which one impregnating element enters the metal due to the reduction of oxide by the carbide and the other—due to thermochemical decomposition of the carbide at the surface of the metal being impregnated. Thus, a borosiliconized layer can be obtained in two ways:

1) by the reduction of sodium monosilicate by boron carbide (B_4C);

2) by the reduction of $Na_2SiO_3 + Na_2B_4O_7$ by silicon carbide (SiC).

In the first case active atoms of silicon are formed during chemical reduction of silica by boron carbide, which is also the diffusion source of boron.

In the second case, active atoms of boron are the result of a reduction of borax by carborundum. SiC acts as the diffusion source of silicon.

The ratio of active atoms of boron and silicon, formed during the chemical reaction can be varied by altering the quantitative ratio between the constituents of the impregnating mixture, thereby influencing the structure, constituent phases, composition and characteristics of the resultant diffusion layers.

In our investigations, experiments were carried out using melts of the following compositions:

1) $75\%\ Na_2SiO_3 + 35\%\ (SiC + B_4C)$;

2) $75\%\ (Na_2B_4O_7 + Na_2SiO_3) + 35\%\ SiC$.

In the first case silicon carbide was gradually substituted by boron carbide and, in the second, by sodium boromonosilicate. The results obtained are given in Fig. 5 (c, d).

For obtaining a borosiliconized diffusion layer it is necessary that the mass ratio of SiC/B_4C or $Na_2SiO_3/Na_2B_4O_7$ in the melt should be increased up to 4/1.

In case the excess of sodium monosilicate over the quantity of tetraborate is less than four times, the borided layer, formed on the surface of steel, does not differ from a 'normal' borided diffusion coating. In baths containing sodium monosilicate along with both the carbides ($SiC+B_4C$), the optimum requirement for borosiliconizing is that there should be a considerable quantitative predominance of carborundum over boron carbide. This is necessary, not only because when this condition is violated the diffusion layer is hardly different from a normal borided layer, as far as structure and properties are concerned, but also in view of the fact that maintaining a high quantitative ratio of $SiC/B_4C=4/1$ helps in significantly improving the thickness of the diffusion saturated layer. The following bath compositions can be considered optimal for borosiliconizing.

1) $65\%\ Na_2SiO_3+7\%\ B_4C+28\%\ SiC$,

2) $35\%\ SiC+52\%\ Na_2SiO_3+13\%\ Na_2B_4O_7$.

The structures of borosiliconized diffusion coatings obtained in both these baths of optimal compositions have been found to be practically identical.

On diffusion saturation of Armco iron, the typical diffusion coating formed consists of a layer of solid solution of silicon in α-iron and two boride layers, one of which is located at the surface of the metal being impregnated forming continuous thin laminate and the other exists beneath the layer of the solid solution of silicon in α-iron (Fig. 58).

Increase in the boron-bearing component in the melt—borax or boron carbide—shifts the structure toward larger volumes of boride phases and reduces the quantity of solid solution of silicon in α-iron. Moreover, the boride phases in the borosiliconized layer are represented, practically, by only one boride, Fe_2B. The proportion of FeB in the diffusion layer, under the conditions of our investigation, was not very high. The borosiliconized layers containing needles of Fe_2B were texturized as compared to the diffusion front.

The diffusion layer formed on boroaluminizing medium carbon steels is somewhat different from that described above. In this case, a more or less thick (few tens of microns) continuous borided layer is formed on the surface of steel, without the typical 'acicular' structure. Beneath the continuous borided layer, there exists equiaxial grains of Fe_2B, more or less uniformly dispersed in the layer of solid solution of silicon in α-iron. The quantity of boride particles, dispersed in the layer of α-solid solution of silicon in iron decreases with increasing depth of the diffusion layer. X-ray diffraction studies

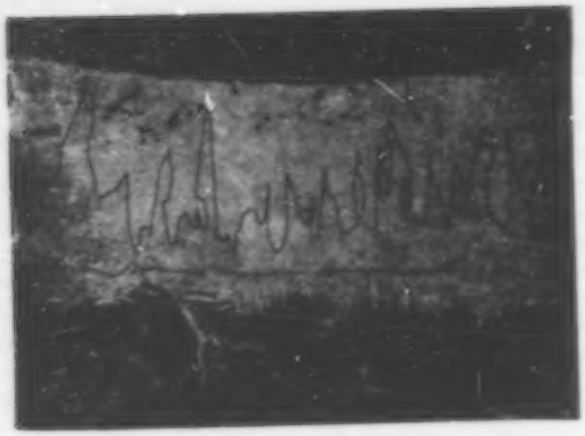

Fig. 58. Microstructure of diffusion layer on medium carbon steel after borosiliconizing. ×200 (for impregnation regime and bath composition see Fig 18).

of diffusion coatings on steel 45 has confirmed the presence of silicide of iron—Fe_5Si_3 along with α-phase and Fe_2B in the surface layer.

The process of formation of a diffusion coating is accompanied by displacement of carbon from the diffusion layer into the volume of the metal. Redistribution of carbon in low-carbon steels leads to the formation of a carbon enriched 'transition zone'. In high-carbon steels, the process of redistribution of carbon is accompanied by a precipitation of boron-carbide inclusions located mainly at the grain boundaries of former austenitic grains, beneath the solid solution of silicon in α-iron.

Kinetic curves showing the variation in thickness and constituent phases of diffusion layers formed at different melt compositions with the change in parameters of electrolysis, were constructed on the basis of data available from metallographic analysis. Results of the investigations on the effect of current density on thickness of the diffusion layer are given in Figs. 59 and 60 (at 950°C and 1000°C, respectively) and Figs. 61 and 62 (at 1050°C).

Electrolysis of melts of the $Na_2B_4O_7$–Na_2SiO_3 system containing 10 to 30% of sodium monosilicate at 950°C results in the formation of borided diffusion layers (Fig. 59). The maximum thickness of the layer formed with a variation in the bath composition changes from 0.12 mm for electrolysis of pure borax to 0.14 mm for a borax melt containing 30 wt.% of sodium monosilicate. The optimum current density decreases from 0.2–0.25 to 0.15 A/cm². Such an effect of introduction of sodium monosilicate in borax melts can be explained by the fact that it is apparently accompanied by a fall in the visco-

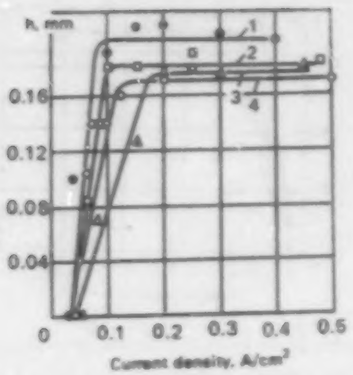

Fig. 59. Variation in thickness of diffusion layer on steel 45 with current density at 950°C:

1—70% $Na_2B_4O_7$ + 30% Na_2SiO_3; 2—80% $Na_2B_4O_7$ + 20% Na_2SiO_3; 3—90% $Na_2B_4O_7$ + 10% Na_2SiO_3; 4—100% $Na_2B_4O_7$.

sity of the melt owing to an increase in the Na_2O content of the melt. Further, it should be noted that a discharge of Si^{+4} ions on the cathode is possible in these melts, which can also participate in the growth of the borided layer.

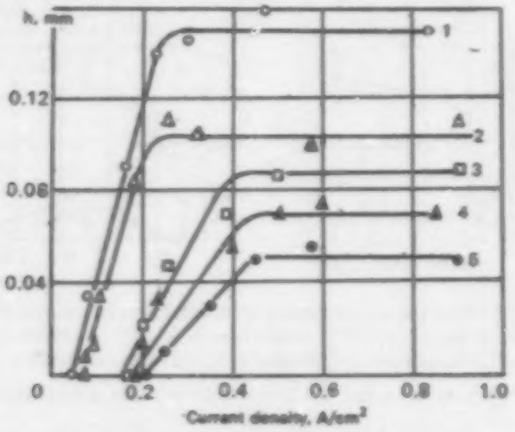

Fig. 60. Effect of current density on thickness of diffusion layer on steel 45 ($t = 1000$°C):

1—50% $Na_2B_4O_7$ + 50% Na_2SiO_3; 2—30% $Na_2B_4O_7$ + 70% Na_2SiO_3; 3—25% $Na_2B_4O_7$ + 75% Na_2SiO_3; 4—20% $Na_2B_4O_7$ + 80% Na_2SiO_3: 5—15% $Na_2B_4O_7$ + 85% Na_2SiO_3.

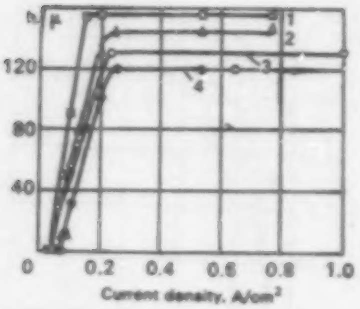

Fig. 61. Variation in thickness of diffusion layer with current density: ($t = 1050$°C. Legend same as in Fig. 59).

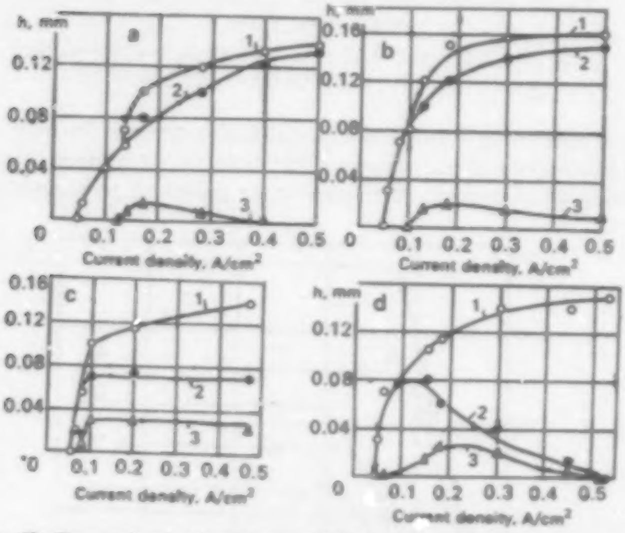

Fig. 62. Current density dependence of thickness and constituent phases of diffusion layers (at 1050°C). Na_2SiO_3 with (a) 10% $Na_2B_4O_7$; (b) 20% $Na_2B_4O_7$; (c) 30% $Na_2B_4O_7$; and (d) 40% $Na_2B_4O_7$:

1—Boride zone on surface; 2—Zone of solid solution of silicon in α-iron; 3—Boride zone.

The structure of borided diffusion layers on steel 45 produced by the electrolysis of borax melts containing 30% and 50 wt.% sodium monosilicate at 950°C are shown in Fig. 63. As regards structure, these layers differ little from diffusion coatings obtained by electrolytic boriding in borax melts.

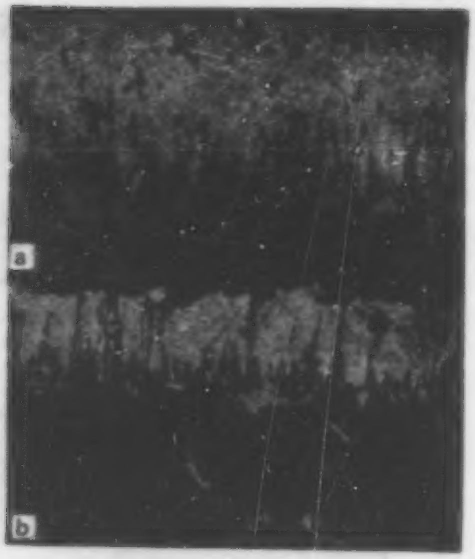

Fig. 63. Microstructure of borided diffusion layers on steel 45:
($t=950°C$, $\tau=30$ min, $j=0.3$ A/cm^2).
Melt: a—30% Na_2SiO_3 + 70% $Na_2B_4O_7$; b—50% Na_2SiO_3 + 50% $Na_2B_4O_7$, ×200.

Electrolysis of melts containing 15–50 wt.% of borax (see Fig. 60) at moderate current densities ($t=950°C$) results in the formation of siliconized layers on the cathode (a layer of α-solid solution of silicon in iron).

On increasing the current density during electrolysis of these melts a borosiliconized layer is formed. The quantity of the boride phases in the diffusion layer increases with the rise in current density as well as in the concentration of borax in the melt. The structure of the borosiliconized layer obtained by electrolysis of the melt, containing 15 wt.% of borax, is shown in Fig. 64. The diffusion layer obtained at a moderately high current density (0.35–0.45 A/cm^2), has the structure of α-solid solution of silicon (and, possibly of boron) in iron, in which boride needles partly misoriented are wedged in from the surface. Medium size boride inclusions are observed in the zone of the interface between the solid solution of silicon in α-iron and the substrate. At a current density of 0.9 A/cm^2 a continuous borided layer is formed from the surface with needles of boride wedging into the solid solution of silicon in α-iron.

As can be seen from Fig. 60, the aggregate thickness of a borosiliconized layer is reduced with a decreasing concentration of borax in the melt from

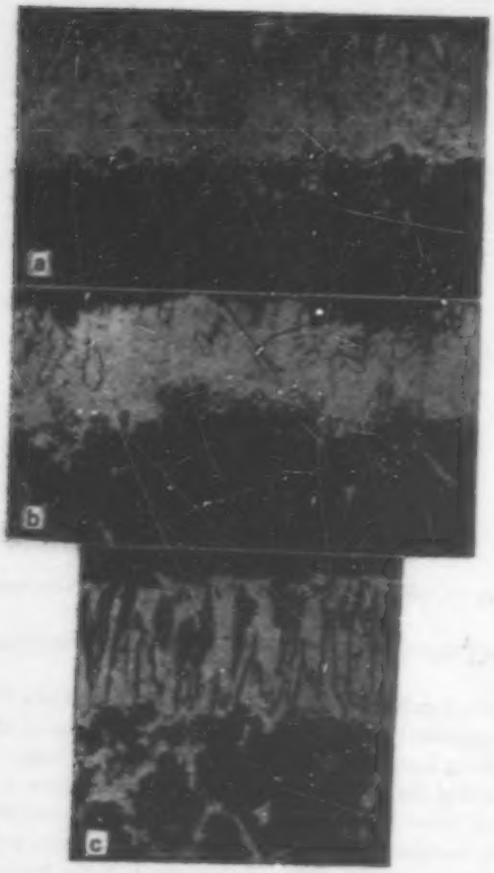

Fig. 64. Microstructure of borosiliconized diffusion coatings on steel 45, obtained by electrolysis of melt containing 15% of borax:

$t = 950°C$, $\tau = 30$ min. Current density, j— a—0.35 A/cm^2; b—0.45 A/cm^2; c—0.9 A/cm^2, ×200.

50 to 15 wt.%. Simultaneously, the optimum current density increases from 0.25 A/cm^2 for a melt with 50 wt.% of borax to 0.50–0.55 A/cm^2 for a melt with 15 wt.% of borax. Similarly, the critical current density also increases from 0.04 to 0.18 A/cm^2.

Increasing the impregnation temperature up to 1050°C leads to a change in structure of the diffusion layers.

Electrolysis of melts with high concentrations of borax results in the formation of borided coatings on the surface of specimens. It can be assumed that, during electrolysis at high current densities, providing for the precipitation of Si^{+4} ions at the cathode, both the borides are alloyed with silicon.

The overall thickness of the borided layer is slightly increased on introduction of sodium monosilicate up to 30 wt.% in the borax melt (see Fig. 61). (This also happens in the case of electrolysis at 950°C.) Any further increase in Na_2SiO_3 content of the melts results in a reduction in the thickness of the diffusion saturated coating. The structure of siliconized layers obtained in melts with 90, 80 and 70 wt.% of borax is shown in Fig. 65. It is observed

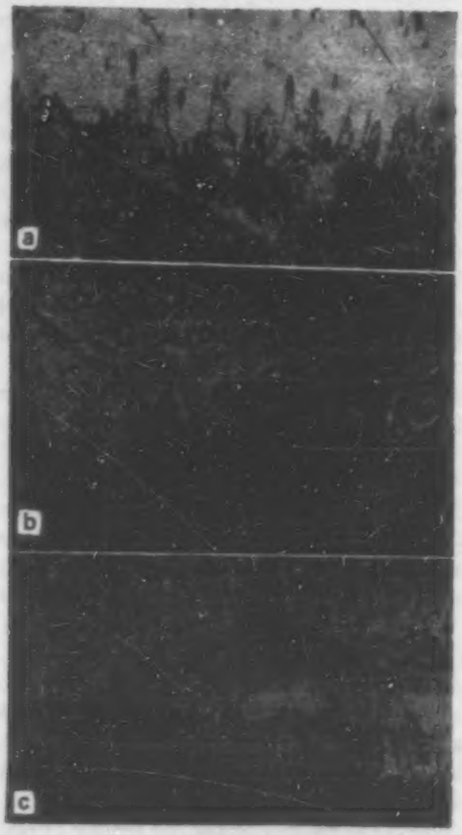

Fig. 65. Microstructures of borosiliconized layers on steel 45 obtained by electrolysis of melts containing (a) 90%; (b) 80% and (c) 70% of borax ($t=1050$°C, $\tau=30$ min, $j=0.2$ A/cm^2), ×200.

that, on increasing the concentration of sodium monosilicate in the melts, there is a rise in the quantity of the eutectic constituent in the diffusion layer.

The diffusion layer, formed on electrolysis of melts with 10, 20, 30 and 40% of borax, generally consists of three zones. A borided zone (continuous) exists on the surface beneath it a zone of solid solution of silicon in iron; and a third zone, i.e. a borided zone is located under the solid solution of silicon in iron at the interface with the bulk. The critical current density of these melts as well as for Na_2SiO_3 melt is 0.05–0.06 A/cm^2 (see Fig. 62). The aggregate thickness of the diffusion layer increases with an increase of current density, whereas the maximum growth corresponds to a variation in the current density of from 0.05 to 0.1 A/cm^2. A further increase in current density is accompanied by a reduction in the rate of growth of the layer (the slope of the plot of variation of thickness of the diffusion layer with current density decreases).

Variation in the composition of the bath changes the proportion of the phases in the diffusion layer. Thus, electrolysis of a melt containing 10% of borax at a current density of 0.5 A/cm^2 leads to the formation of a borosiliconized coating with a very thin borided zone at the surface of the specimen. The thickness of the borided zone increases with an increase in the borax content. A borided diffusion coating with a small laminate of silicon ferrite is formed in melts containing 40 wt.% of borax. Electrolysis of these melts (with 40 wt.% of borax) at lower current densities results in the formation of diffusion coatings with three zones (two borided zones separated by an α-solid solution of silicon in iron).

The variation in thickness and structure of diffusion layers with bath composition (Na_2SiO_3–$Na_2B_4O_7$ system) at 950°C and current density of 0.8–0.9 A/cm^2 and at 1050°C and current density of $\approx$0.5 A/cm^2 is shown in Fig. 66. The location of the maximum on these curves corresponds to the borax content of melts of between 60 to 70 wt.%. At 1050°C, a siliconized coating is formed in melts containing up to 10 wt.% of borax. On electrolysis of melts containing more than 50 wt.% of borax, a borided diffusion coating is formed on a steel cathode. A borosiliconized layer is formed in melts containing 10 to 50 wt.% of borax, and the amount of α-solid solution of silicon (and possibly boron) in iron increases at higher temperatures.

The position of the maximum on the plot of thickness of diffusion layer vs composition of the bath at 1050°C corresponds to 20 to 40 wt.% of borax in the melt. The appearance of the maximum can be attributed to the change in structure of the diffusion impregnated layers owing to variations in composition of the melt in this zone.

The composition of the electrolyte and the regime of electrolysis for producing a diffusion layer of the desired thickness and structure can be selected with the help of the phase diagram in conjunction with the kinetic curves

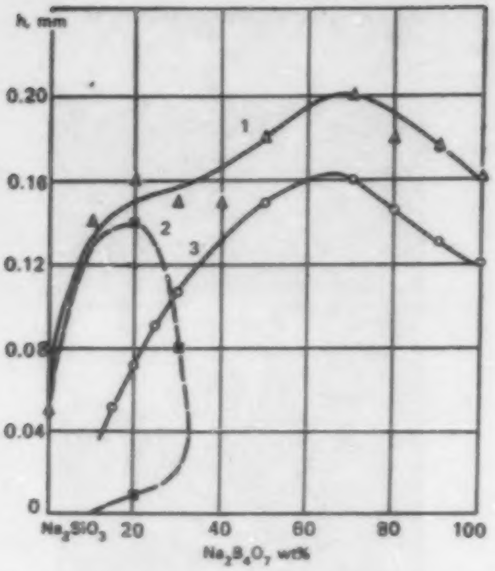

Fig. 66. Variation of thickness and structure of diffusion layers with composition of the melt:

1—Borided layer; 2—Layer of solid solution of silicon in α-iron (t=1050°C); 3—Borided layer (t=950°C).

which show the variation in thickness and phases in the diffusion layers with changes in current density.

The microstructures of borosiliconized layer on steel 45, obtained by diffusion saturation at 1000°C with durations of treatment varying from 1.2 to 3 h, are shown in Fig. 67. As can be seen from the figure, on increasing the duration of treatment the proportion of phases in the diffusion layer is preferentially of borides.

The variation in the thickness of borosiliconized coatings on steel 45 with a change in duration of the treatment at 950°, 1000° and 1050°C is shown in Fig. 68.

On borosiliconizing of Armco iron and carbon steels, diffusion-saturated coatings with different proportions of phases are formed on the surfaces of specimens (borides and α-solid solution of silicon in iron). The structure of these phases is determined by the composition of the bath, temperature and duration of the surface-alloying process. By varying the impregnation parameters it is possible to obtain diffusion coatings with the desired ratio and distribution of phases along the depth of diffusion layer.

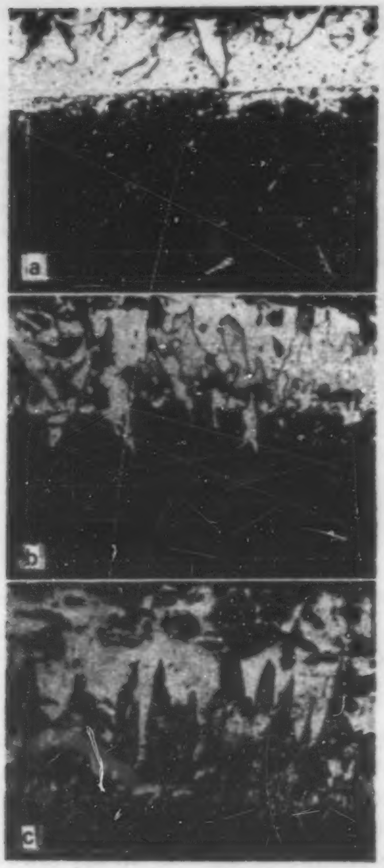

Fig. 67. Microstructure of borosiliconized layers on steel 45:
Melt composition: 15% $Na_2B_4O_7$ + 85% Na_2SiO_3 (t = 1000°C, j = 0.4 A/cm^2,
τ = a—1 h, b—2 h, c—3 h, × 120).

The dependence of the total thickness of a diffusion layer and proportion of boride phases in the layer obtained by electrolyzing melts containing 20% of borax and 80% of sodium monosilicate, on the carbon concentration in the substrate steel is shown in Fig. 69. Specimens with different carbon contents were subjected to diffusion saturation. Comparison of the results with those obtained for electrolytic boriding shows that on increasing the carbon content the variation in thickness of the diffusion layer is identical during

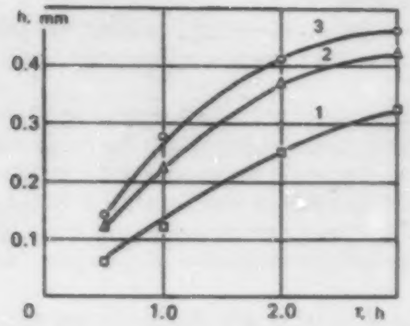

Fig. 68. Effect of duration of treatment of thickness of borosiliconized layers on steel 45:

Temperature: 1—t=950°C, 2—1000°C; 3—1050°C.

boriding and borosiliconizing. However, the quantity of Fe_2B phase during borosiliconizing is more than that in boriding.

The effect of the alloying elements on the kinetics of boriding of medium carbon steels has been studied in detail. It has been established that elements such as aluminum, chromium, tungsten, molybdenum and others reduce the

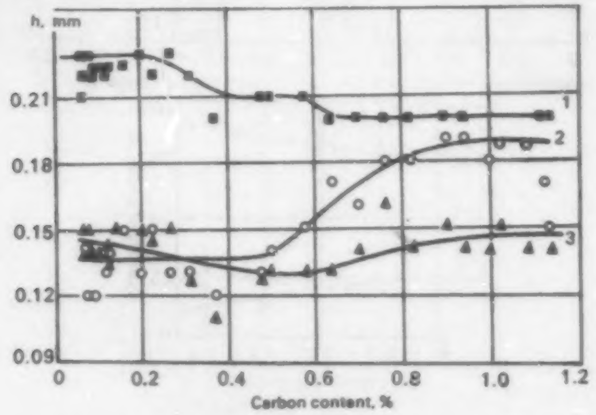

Fig. 69. Variation of thickness of borided layer on concentration of carbon in steel during borosiliconizing in melts containing 80% Na_2SiO_3+20% $Na_2B_4O_7$. t=950°C, τ=2 h:

1—aggregate thickness of layer; 2—thickness of continuous layer of borides; 3—thickness of layer of FeB phase.

thickness of the borided layer, whereas nickel and manganese have practically no effect on this thickness.

Molybdenum, tungsten, chromium, silicon, aluminum, copper and manganese increase the thickness of the siliconized layer while nickel has a negative effect.

Investigations have shown that the introduction of elements which restrict the region of iron, favors an increase in the quantity of solid solution of silicon in iron and a reduction in the amount of boride phases. In such cases, the total thickness of the diffusion layer is reduced. Results of investigations on the effect of molybdenum and chromium on the total thickness of the borosiliconized layer and the proportion of phases in it are given in Fig. 70 (a, b).

The introduction of nickel in steel has hardly any effect on the thickness of the diffusion layer, but the proportion of phases changes, resulting in an increase in boride phase (Fig. 70, c).

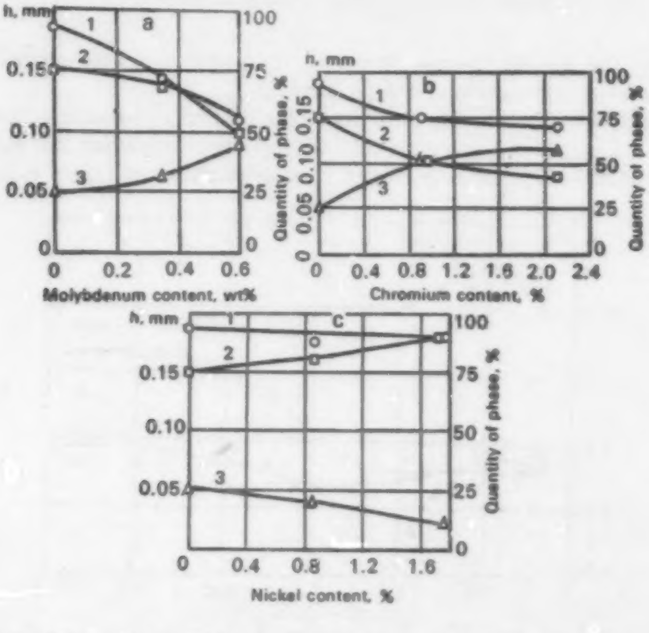

Fig. 70. Effect of (a) molybdenum, (b) chromium and (c) nickel on thickness of borosiliconized layers and proportion of phases in them:

Melt composition: 20% borax + 80% Na_2SiO_3, $t = 1000$°C; $j = 0.4$ A/cm^2.

1—aggregate thickness of layer; 2—amount of borides; 3—amount of solid solution.

Microstructures of siliconized layers on medium carbon alloy steels are shown in Fig. 71.

The properties of borosiliconized diffusion coatings have not been studied in detail.

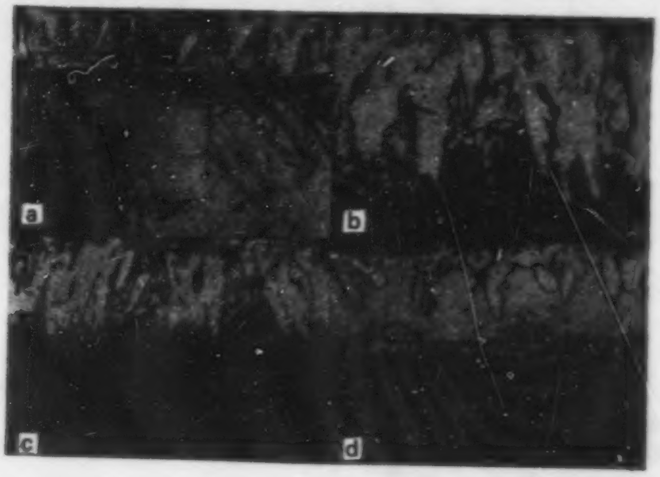

Fig. 71. Microstructure of borosiliconized layers on (a) steel 40Kh; (b) steel 40M; (c) steel 40N2 and (d) steel 40G2.

In [26], it has been pointed out that borosiliconizing in powder mixtures, containing up to 10% of a silicon-bearing component, results in an improvement in the microhardness of borides of iron up to 2200–2300 kgf/mm^2. This has been attributed to alloying of borides of iron by silicon.

However, in our investigations on electrolytic borosiliconizing, quite different results have been obtained. Data from statistical measurement of microhardness of the borides, FeB and Fe_2B, in borided and borosiliconized layers on steel 45 is given in Fig. 72 (measurements were made on PMT-3 at a 100 gf load). The maximums for frequency curves of microhardness of boride FeB coincide in cases of 'pure' boriding and borosiliconizing and correspond to a microhardness of 1850 kgf/mm^2. In borosiliconizing, the maximum of the frequency curve of microhardness of Fe_2B is shifted toward much higher values of microhardness and corresponds to 1550 kgf/mm^2; whereas for 'pure' boride it corresponds to 1350 kgf/mm^2. The results obtained confirm that while the solubility of silicon in Fe_2B is significant, it is practically nil in FeB.

The data from spectral analysis of the surface of borosiliconized specimens, the structure of which revealed a complete absence of boride, FeB, and

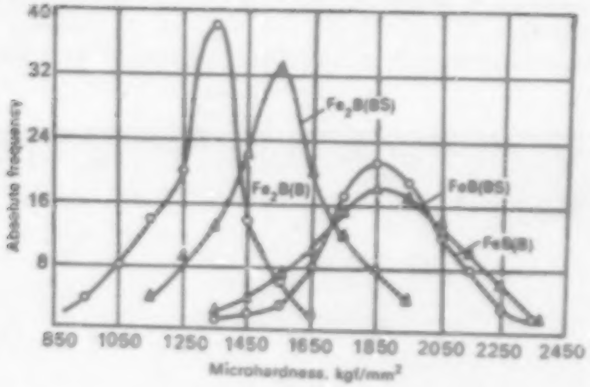

Fig. 72. Results of statistical measurements of microhardness of borides, FeB and Fe_2B, in borided and borosiliconized layers on steel 45.

needles of Fe_2B, forming a continuous layer on the surface of the specimen, confirms the view on alloying of boride, Fe_2B, with silicon during borosiliconizing. In this case the concentration of silicon on the surface of a borosiliconized specimen was found to reach up to 5–7%.

This is further confirmed by results of investigations on the redistribution of silicon during the process of formation of a borosiliconized coating on silicon steels (Fig. 71). Silicon is fully displaced from the zone of boride, FeB, into Fe_2B and further into the zone of α-phase.

Borosiliconizing in powder mixtures, containing 90% of boron-bearing components (84% B_4C + 16% $Na_2B_4O_7$) and 10% of silicon-bearing components (95% Si + 5% NH_4Cl), leads to a greater improvement in relative wear resistance of plain carbon steels during abrasion wear, than boriding in solid mediums (Table 40) [271].

Table 40

Composition of mixture		Thickness of coating, μ		Relative wear resistance	
84% B_4C + 16% $Na_2B_4O_7$	95% Si + 5% NH_4Cl	Steel U8A	Steel 10	Steel U8A	Steel 10
100	—	200	240	4.4	4.2
90	10	185	255	6.8	5.5
75	25	180	200	4.6	3.2
50	50	175	195	5.5	4.0

Thus, while boriding of steel 10 and steel U8A increases their wear resistance during abrasion by 4.2 to 4.4 times, borosiliconizing (in a mixture containing boron-bearing and silicon-bearing components in the ratio of 90 : 10) results in 5.5 and 6.8 fold improvements in wear resistance, respectively.

This phenomenon is most probably related to alloying of the boride, Fe_2B, with silicon and a consequent improvement in its microhardness.

With increase in silicon content of the mixture up to 20% or more, the wear resistance of the layer decreases as compared to that of a borided layer. This has been attributed to reduction in the thickness of the continuous layer of borides and the relatively greater amount of silicide phases in the diffusion layer. Borosiliconizing results in some improvement in the corrosion resistance of steels. Investigations on corrosion resistance were carried out on steel 20. The regime of diffusion saturated coatings are given in Table 41. The duration of testing was 4 days. A 3% aqueous solution of sodium chloride and 10% dilute hydrochloric and sulfuric acids were employed as testing media.

Table 41

Type and regime	Thickness of layer, mm	Microhardness at the surface, kgf/mm²	Relative content of borides in the layer, %
Boriding: $t=950°C$, $\tau=2$ h, current density 0.2 A/cm²	0.20	1700–1900	100
Siliconizing: 95% Na_2SiO_3 + 5% NaF, $t=1050°C$, $\tau=1$ h, current density 0.2 A/cm²	0.13	430	—
Borosiliconizing I: 50% Na_2SiO_2 + 50% $Na_2B_4O_7$, $t=950°C$, $\tau=1$ h, current density 0.4 A/cm²	0.19	—	100
Borosiliconizing II: 50% Na_2SiO_3 + 50% $Na_2B_4O_7$, $t=1050°C$, $\tau=1$ h, current density 0.4 A/cm²	0.21	—	75
Borosiliconizing III: 85% Na_2SiO_3 + 15% $Na_2B_4O_7$, $t=950°C$, $\tau=1$ h, current density 0.4 A/cm²	0.14	—	25
Borosiliconizing IV: 85% Na_2SiO_3 + 15% $Na_2B_4O_7$, $t=1050°C$, $\tau=1$ h, current density 0.4 A/cm²	0.28	—	20

Specimens were drawn from the solutions for testing every day, they were then cleaned of products of corrosion, washed, dried and then weighed. After testing, the specimens were subjected to metallographic investigations.

The results obtained are given in Tables 42–44. From Table 42 it can be seen that borosiliconizing in all the investigated regimes significantly improves the corrosion resistance of steel 20 in a 3% aqueous solution of NaCl (by 3–5 times). The loss in weight of borosiliconized specimens of steel 20 in a 3% aqueous solution of sodium chloride is noticeably less than that of borided or siliconized specimens. However, metallographic analysis has established that in borosiliconized layers, selective corrosion of a particular phase takes place at some isolated locations. In this case only a solid solution of silicon in α-iron is subject to corrosion damage, whereas boride needles are practically unaffected. After penetrating the diffusion layer, corrosion spreads beneath it.

Table 42

Borosiliconizing regime	Weight loss, mgf/cm^2 in steel 20 in 3% aqueous solution of sodium chloride			
	duration of testing, h			
	24	48	72	96
—	0.70	2.50	3.50	4.10
I	0.02	0.48	0.87	1.05
II	0.08	0.48	0.58	1.30
III	0.2	0.34	0.38	0.78
IV	0.34	0.65	0.70	0.80

Table 43

Borosiliconizing regime	Weight loss, mgf/cm^2 in steel 20 in 10% solution of HCl				Conditions of the surface
	duration of testing, h				
	24	48	72	96	
—	82.0	94.5	120.0	132.0	Unsatisfactory
I	8.8	19.8	36.2	78.0	Good
II	8.8	16.7	31.4	66.4	"
III	5.5	12.3	22.0	38.6	"
IV	2.3	9.7	18.2	31.4	"

Table 44

Type of surface treatment	Weight loss, mgf/cm^2, in steel 20 in 10% HCl solution of H_2SO_4				Conditions of the surface
	duration of testing, h				
	24	48	72	96	
—	25.6	54.7	96.2	120.0	Unsatisfactory
Borosiliconizing:					
I	22.2	43.6	64.5	130.0	"
II	26.8	37.1	50.8	87.0	"
III	1.9	5.4	7.7	11.9	Good
IV	4.6	8.5	12.0	22.5	"
Siliconizing	4.4	6.2	9.3	10.4	"
Boriding	12.4	25.8	37.2	43.6	Unsatisfactory

From metallographic investigations it is observed that borosiliconized coatings having a two-phase structure at the surface (borides and solid solution of silicon in α-iron) cannot be recommended for prolonged exposure in aqueous solutions of sodium chloride. From this point of view the borosiliconizing process carried out in the boriding regime producing a matrix of boride phases appears to be promising. This type of coating can be produced either in melts containing up to 30% of Na_2SiO_3 (balance borax) or in a powder mixture containing less than 10% of silicon. Coatings obtained in these impregnating mediums has a 20 to 30% higher corrosion resistance in a 3% aqueous solution of sodium chloride than a 'pure' borided coating. These coatings are especially effective under simultaneous conditions of corrosion and abrasion in the environment. Borosiliconized coatings obtained by employing the 5th and 6th diffusion-saturation regimes (see Table 41) are similar to siliconized coatings with regard to their service properties in solutions of sodium chloride.

Tests in 10% aqueous solutions of hydrochloric acid have shown that borosiliconized coatings offer reliable protection to steel 20 from corrosion (on diffusion saturation their corrosion resistance increases by 2–4 times) (Table 43). However, in this medium, they are less effective than borided coatings, and are not recommended for practical application.

The maximum corrosion resistance in an aqueous solution of sulfuric acid is that of siliconized layers (Table 44).

Borosiliconized layers, obtained on using regime 5, have a corrosion resistance similar to siliconized layers. However, as the relative content of boride phases in these coatings is not large, they do not offer any advantages over siliconized layers.

Borided, siliconized and borosiliconized diffusion coatings fail to protect plain carbon steels from corrosion in 10% dilute nitric acid.

The heat resistance of diffusion saturated layers were studied at 700°, 800° and 900°C in a muffle furnace, in air. Studies were conducted on 40Kh and 1Kh18N9T steels. The duration of the test was 25 h. After every 5 h the crucible containing the specimens was drawn from the furnace and cooled to 150–100°C. The specimens were then stored in a desiccator and allowed to cool to room temperature. The degree of heat resistance was evaluated according to the weight gain. Specimens were diffusion saturated according to the regime mentioned in Table 41. The results of diffusion saturation are given in Table 45, and those of investigations on heat resistance, in Table 46. As can be seen from the data borosiliconizing protects structural steels from corrosion up to 800°C to the same extent as boriding or siliconizing.

Table 45

Type of treatment	Grade of steel	Layer thickness, mm	Microhardness of surface, kgf/mm²	Relative content of boride phase in coating, %
Boriding	40Kh	0.14	1700–1900	100
	1Kh18N9T	0.10	1900–2000	100
Siliconizing	40Kh	0.14	620	—
	1Kh18N9T	0.09	600	—
Borosiliconizing:				
I	40Kh	0.20	—	100
	1Kh18N9T	0.12	—	100
II	40Kh	0.23	—	50
	1Kh18N9T	0.13	—	50
III	40Kh	0.12	—	15
	1Kh18N9T	0.10	—	3–5

It should be noted that borosiliconizing proved to be an effective method for improving the heat resistance of 1Kh18N9T steel. Borosiliconized specimens of this steel, with borides on the surface and α-solid solution in contact with the core metal (3rd and 4th regimes of borosiliconizing, Table 41) had a much higher heat resistance than borided specimens. Specimens prepared according to 5th regime of borosiliconizing providing for the formation of a solid solution with iron at the surface and fine acicular borides beneath α-solid solution distributed along the boundaries of austenitic grains, had a better heat resistance than siliconized specimens of 1Kh18N9T steel.

A superiority of borosiliconized diffusion coatings on plain carbon steel as compared to borided coatings, with respect to heat and corrosion resistance has also been reported in [271].

Table 46

Grade of steel	Type of treatment	Weight gain of specimens, mg/cm² on testing for, h														
		5			10			15			20			25		
		t			*t*			*t*			*t*			*t*		
		700	800	900	700	800	900	700	800	900	700	800	900	700	800	900
40Kh	—	3.7	8.6	37.5	4.4	16.0	41.3	6.3	20.9	43.5	8.5	25.2	48.4	9.6	31.3	52.0
1Kh18N9T	—	0.23	0.26	4.1	0.34	0.38	5.8	0.43	0.50	6.2	0.62	0.72	7.3	0.73	0.85	8.0
40Kh	Boriding	2.3	5.2	35.0	2.9	5.8	56.0	4.4	9.4	66.0	5.7	12.7	73.2	6.5	19.7	77.3
1Kh18N9T		0.18	0.21	2.9	0.25	0.31	4.0	0.32	0.40	4.2	0.38	0.47	4.8	0.45	0.50	5.7
40Kh	Siliconizing	2.2	6.3	13.1	—6	9.8	19.0	3.8	17.2	21.0	5.4	18.1	22.0	6.5	19.4	22.5
1Kh18N9T		0.27	0.30	0.7	0.28	0.33	0.9	0.30	0.43	1.2	0.33	0.45	1.6	0.35	0.45	2.0
40Kh	Borosiliconizing—I	3.3	11.1	58.1	5.4	14.8	67.2	5.8	24.3	79.0	66	30.1	84.8	7.2	58.1	94.5
1Kh18N9T		0.16	0.37	2.6	0.23	0.41	4.3	0.27	0.44	4.8	0.35	0.50	5.1	0.43	0.52	6.2
40Kh	Borosiliconizing—II	3.4	10.5	41.8	4.2	16.2	69.0	4.9	23.0	73.4	5.5	30.3	80.0	6.5	38.5	87.6
1Kh18N9T		0.20	0.33	2.4	0.25	0.37	3.9	0.36	0.42	4.7	0.40	0.49	5.3	0.45	0.54	6.7
40Kh	Borosiliconizing—III	3.1	7.2	43.2	4.1	12.1	53.6	4.6	16.6	63.1	5.8	18.9	71.2	6.4	23.4	74.1
1Kh18N9T		0.15	0.15	0.5	0.17	0.20	1.0	0.17	0.22	1.2	0.18	0.25	1.4	0.20	0.27	1.5

Borosiliconizing in pulverized mixtures significantly improves the corrosion-fatigue resistance of steels (Table 47) [271]. These results are similar to those obtained in the case of boriding. The comparatively low values of the fatigue limit are due to the low strength of the steel. The effectiveness of these coatings, in improving the corrosion fatigue resistance, increases with an increase in the strength of the base metal. A considerable increase in the corrosion-fatigue resistance of steel, as a result of borosiliconizing, is explained by the authors [271], on the basis of generation of a high degree of residual compressive stresses in the diffusion-saturated coatings and an increase in the corrosion resistance of borosiliconized coatings.

Table 47

Type of treatment	Fatigue limit, kgf/mm^2	
	in air $N=10^7$ cycles	in 3% solution of NaCl, $N=2\times10^7$ cycles
Untreated (normalizing from 950°C)	20.5	9.25
Boriding ($t=950$°C, $\tau=6$ h)	23.5	12.5
Borosiliconizing ($t=950$°C $\tau=6$ h)	22.5	16.5

Subsequent tempering of specimens after diffusion saturation of steel with boron and silicon leads to a reduction in the fatigue limit, which is attributed to the change in flow lines of compressive stresses and, in many cases, to the appearance of cracks in the diffusion layer during heat treatment.

The appearance of cracks in a diffusion coating during heat treatment should be attributed more to faults in production of the diffusion coating rather than to the properties of the coating itself.

2. BOROCHROMIZING

Simultaneous diffusion saturation of steels with boron and chromium can be achieved by electrolytic [80, 83, 321, 322] as well as electroless liquid [323] processes. According to the data of Samsonov et al. [24], multicomponent saturation of steel with boron and chromium from powders of elements or their ferroalloys cannot be achieved. On borochromizing in mixtures containing up to 70% of chromium, a preferred boriding takes place while in mixtures with a 90% or higher chromium content because chromizing occurs. In the chromium concentration interval from 70 to 90% a diffusion saturated layer is not formed. This is attributed to the interaction of the diffusing species in the impregnating mixture.

Electrolytic borochromizing is carried out in borax melts with additions of chromic oxides or in melts of the B_2O_3–Cr_2O_3 system with the introduction of different diluents: oxides or salts of alkali metals. For example, Pasechnic et al. have recommended [83] the following composition of an electrolyte:

$$3\text{–}8\%\ Cr_2O_3 + 75\text{–}80\%\ B_2O_3 + 22\text{–}12\%\ NaF.$$

In our investigations the concentration of Cr_2O_3 varied between 10 to 50% (balance borax). In [80, 83, 321], electrolytes with lower concentrations of chromic oxide have been investigated.

Specimens were connected in series with the electrolyte to act as a cathode, and a graphite rod served as an anode.

The results obtained at 950° and 1050°C are given in Fig. 73 in the form of a plot of the phases formed at different compositions of the melt and applied voltage (points on plots correspond to 1050°C only). Lines 1 and 2 on the plot correspond to the beginning of deposition of chromium and boron, on the cathode, respectively.

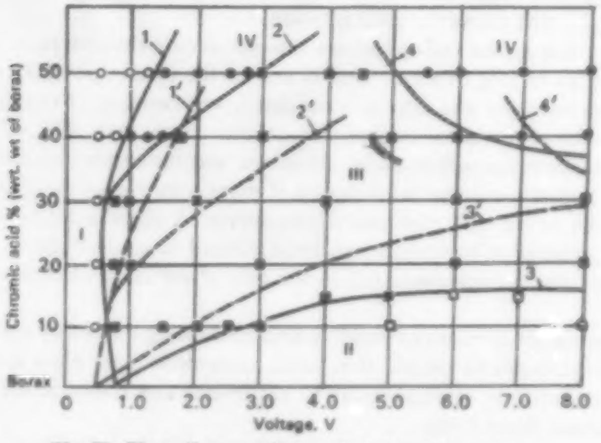

Fig. 73. Phase diagram of electrolytic borochromizing.

Lines 3 and 4 isolate the zones of boriding and chromizing from the zone of simultaneous diffusion saturation of iron with chromium and boron. A diffusion coating does not exist in zone I. In zone II, the diffusion layers (externally) do not differ from those obtained during 'pure' boriding and consist of borides of iron, FeB and Fe_2B, alloyed with chromium. In the zone of chromizing (IV) the diffusion-saturated layer formed on iron comprises solid solutions of chromium and boron in α-iron, whereas on steel the coating is of a carbide type $(Cr, Fe)_{23}C_6 + (Cr, Fe)\ 7C_3$. Complex coatings are formed in zone III. These coatings consist of solid solutions of boron and chromium in α-iron and boride of chromium (possibly alloyed with iron).

The data on constituent phases of diffusion-saturated layers given in [83] do not, however, tally with the description given above. On the basis of x-ray diffraction studies, the authors consider that the following phases coexist in the diffusion-saturated layer: $(Cr, Fe)_{23}C_6$, FeB, Fe_2B, CrB_2, Cr_2B, Cr_5B_3.

This needs, perhaps, some clarification. For example, by varying the composition of the electrolyte and the parameters of electrolytic diffusion coating, it is possible to obtain coatings ranging from 'pure' chromized to pure borided layers with a wide range of borochromized layers distinguished by the ratio of boride phases and solid solutions in the resultant diffusion layer.

The deposition potentials for chromium and boron in melts containing up to 30% Cr_2O_3 are very close to each other and remain practically unchanged during variations in the chromic-oxide content in the melt. Diffusion layers obtained by impregnation in the aforementioned electrolytes, as indicated earlier, have a two-phase structure and consist of a solid solution (chromium and boron in iron) and borides of chromium (possibly, alloyed with iron) located above the solid solution.

An increase in the voltage across the cell during electrolysis of the bath containing up to 15% of Cr_2O_3 results first in the formation of a two-phase borochromized layer and later in a borided layer consisting of borides of iron (alloyed with chromium). In melts containing more than 30% of chromic oxide the deposition potentials of chromium and boron are different. Moreover, the deposition potential of boron is more sensitive to variations in the composition of the melt than that of chromium. A slight increase in the deposition potential of chromium can be attributed to an increase in viscosity of the melt and a consequent fall in the rate of diffusion of chromium ions in it.

The existence of zones of boriding and chromizing limited by curves 3 and 4, can be attributed to the fact that, here, electrolysis takes place in the mode of a limiting current corresponding to chromium and boron in the first and second zones, respectively.

Along with the results obtained at 1050°C (solid lines) the data of investigations at 950°C (dashed lines) has also been given for the sake of comparison in Fig. 73. From the given data, it can be seen that the rise in the saturation temperature widens the zone of simultaneous surface impregnation of iron with boron and chromium. The zone of pure chromizing also widens to some extent, at the cost of the zone of 'pure' boriding. The beginning of the zone of pure chromizing (with a rise in the saturation temperature) shifts upwards with the concentration of chromic oxide in the melt, from 20% (of the weight of borax) to 30%. Qualitatively, the characteristics at 1050°C are also maintained at 950°C.

With an increasing content of chromic oxide in the melts, the thickness and microhardness of diffusion-saturated layer continue to decrease whereas the concentration of chromium increases [83].

The effect of the duration of treatment and the magnitude of the external electromotive force (cathodic current density) on the variation of structural constituents and thickness of the diffusion layer are given in Figs. 74 and 75.

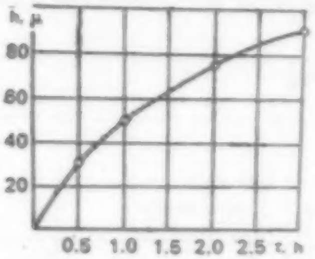

Fig. 74. Effect of duration of treatment on thickness of borochromized layer on steel 45 at 1050°C.

Using phase diagrams as well as the data on the kinetics of formation of coatings, it is possible to select an appropriate composition of the melt and the saturation regime in order to obtain a desired composition in a diffusion layer.

In addition to the electrolytic method for production of borochromized diffusion layers a successful electroless liquid method has also been reported. Diffusion coating is carried out in melts of the same composition, as those used for electrolyte borochromizing, but with the addition of appropriate

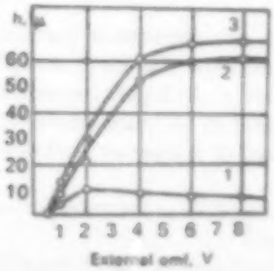

Fig. 75. Effect of external emf on thickness and constituent phases of borochromized layer on steel 45:

$t=1050°C$, $\tau=3$ h.

1—chromized layer; 2—borided layer; 3—total thickness of diffusion-saturated layer.

reducing agents. Calcium silicide can be used as one such agent. The dependence of the thickness of diffusion-saturated coatings on the ratio of borax and chromic oxide in the melt, at a constant, optimum concentration of calcium silicide (15 wt.%), is shown in Fig. 76. Zones of typical diffusion coatings are also indicated in the figure. Borochromizing was carried out for 3 h at 1050°C. At low concentrations of Cr_2O_3 (up to 5%) in the melt, a typical borided layer is formed. (To a limited extent, it may be alloyed with chromium.)

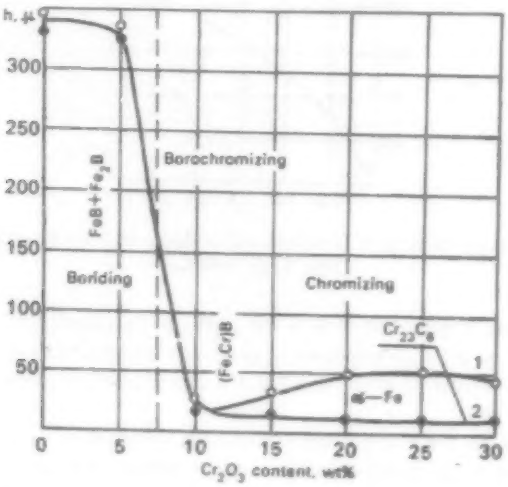

Fig. 76. Variation in thickness of diffusion layer with composition of mixture in liquid borochromizing of (1) Armco iron and (2) steel 45.

In cases where the Cr_2O_3 concentration in the melt is 5–15%, the diffusion layer consists of complex borides, (Fe, Cr)B and $(Fe, Cr)_2B$, and its total thickness varies between 5–10 μ. At higher concentrations of chromic oxide, the process gradually transforms to 'pure' chromizing. On iron a layer of α-solid solution and on steel 45 a layer of carbides of the type ($Cr_{23}C_6$+ Cr_7C_3) are formed.

The surface hardness, according to the results of our investigations, ranges between 2200–2300 kgf/mm².

Much lower values of hardness—1700–1900 kgf/mm² have been reported by Pasechnik et al. [83].

The characteristics of borochromized diffusion coatings have not been fully studied. Pasechnik et al. [321] have indicated that simultaneous surface alloying of steels with boron and chromium ensures diffusion-saturated layers which are much more 'elastic' than borided diffusion.

Similar data is given in [83]. The degree of brittleness was estimated according to the force required for 'chipping' of the diffusion layer along the edge of a square-section specimen. This force is 200–250 kgf for borochromized steels and 150 kgf for borided steels.

High wear-resistant characteristics of borochromized steels are reported in [83, 321]. The wear resistance of steel 45 is 9 times higher in the borochromized state than that obtained after heat treatment (HRC 26-28).

An industrial evaluation of the borochromizing process has been carried out at the synthetic fiber plant at Kursk (borochromizing of holders of heating elements of spinning machines is undertaken to improve their durability). These components are subjected to abrasive wear. Normal electrolytically chromium-plated holders can be used only for 2–3 days till the strain-hardened coating is worn out. Borochromized holders served for more than two months, and there was also an improvement in the quality of the fiber.

As [321, 324] do not provide any data on comparison of the costs of borided and borochromized articles, it is not possible to draw any conclusion in regard to the advantage of using one or other process of strengthening.

3. BOROTUNGSTENIZING AND BOROMOLYBDENIZING

Simultaneous diffusion saturation of carbon steels with boron and molybdenum or tungsten is carried out in melts of borax with additions of sodium molybdate or sodium tungstate (Na_2MoO_4 or Na_2WO_4) at 950–1100°C and at current densities in the range of 0.05 to 0.55 A/cm^2 [323]. A complete range of compositions from pure borax to 100% molybdate (or tungstate) was investigated (at intervals of 10%).

A plot of the phases formed at different compositions of the mixture and current densities used during electrolysis has been drawn on the basis of available data (Fig. 77). It indicates the necessary conditions for the formation of any type of diffusion coating.

Metallographic studies of the structure of resulting coatings and changes in their hardness help in establishing the regions in which layers of uniform structure are formed.

The plot of the constituent phases formed during electrolytic boromolybdenizing (tungstenizing) confirms the formation of layers of only two types: borided and molybdenized (tungstenized). Borided diffusion-saturated coatings consist of borides, FeB and Fe_2B (probably alloyed, to some extent, with molybdenum or tungsten.) In the central range of concentration, no diffusion layer is formed. Apparently, during electrolysis of melts of these compositions, the amount of atoms of boron and molybdenum or tungsten deposited at the cathode correspond to the stoichiometric compositions of borides of molybdenum and tungsten. These borides are formed in the cathode and hence do not participate in the formation of the diffusion layer. The proper-

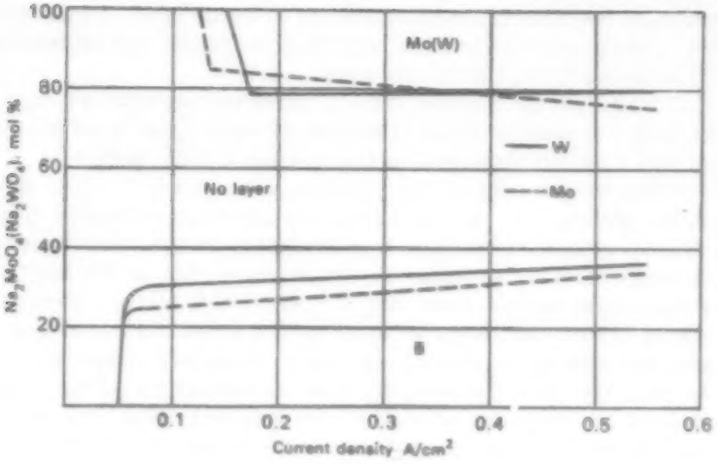

Fig. 77. Plot or phases formed at different compositions of mixture and current densities employed during simultaneous electrolytic saturation with boron and molybdenum (or tungsten):
$t = 1000$°C, $\tau = 1$ h.

ties of borided coatings, obtained in the presence of up to 30–35% Na_2MoO_4 (Na_2WO_4) have not been studied.

4. BOROTITANIZING

Simultaneous surface alloying of steel components with boron and titanium can be carried out either in powders of titanium and boron-bearing materials with additions of activators [23], or by electrolysis of melts of the $Na_2B_4O_7$–TiO_2 system [321]. In the first case, most often, powder mixtures based on boron carbide and ferrotitanium (pure titanium) are employed. For example, the active mixture used by Geraseva et al. [23] for diffusion saturation with boron and titanium mainly consisted of boron carbide, ferrotitanium (47% Ti), borax, ammonium chloride and sodium chloride (Table 48) [23].

The thickness and microhardness of diffusion layer reduces with a rise in the ferrotitanium content of the impregnation mixture. A minimum thickness was obtained in a mixture containing 65% of ferrotitanium. At lower concentrations of titanium a preferred boriding and, at higher concentrations, a preferred titanizing occurs. Intensive decarburizing of the steel surface takes place at 60–65% of ferrotitanium in the mixture.

Table 48

Composition of mixture for borotitanizing, wt. %					
B_4C	$Na_2B_4O_7$	NaCl	NH_4Cl	Al_2O_3	Ferrotitanium
77.4	14.75	1.39	1.16	1.25	3.75
73.6	14.0	1.3	1.1	2.5	7.5
61.3	11.685	1.1	0.915	6.25	18.75
40.9	7.75	0.74	0.61	12.5	37.5
20.45	3.875	0.37	0.305	18.75	56.25
8.175	1.557	0.146	0.122	22.5	67.5
4.09	0.775	0.074	0.061	23.75	71.25

Similar results on the kinetics of formation of borotitanized diffusion coatings as a function of composition of the impregnating mixture were obtained during investigations on creep-resistant ZhS6K alloy [20, 325]. A minimum thickness of the diffusion coating was obtained at 50% Ti. This phenomenon is attributed to interaction between boron and titanium in the impregnating mixture. The presence of boride, TiB_2, has been established [325] by x-ray diffraction analysis of processed mixtures corresponding to the minimum on the plot of thickness of the layer versus composition of the mixture. In this connection it is important to note that the minimums for commercial iron and ZhS6K alloy have different values, which should not be the case if these were determined only by the processes of interaction between the diffusants in the charge. As indicated earlier, interaction of the diffusing agent with the substrate metal and among themselves in the diffusion layer plays a significant role in the process of formation of complex diffusion coatings. Electrolytic borotitanizing is carried out in $Na_2B_4O_7$–TiO_2 melts at 950–1050°C and at current densities of 0.2–0.4 A/cm^2.

The characteristics of borotitanized diffusion layers have not been studied in detail. From the data reported by Geraseva et al. [23] it follows that a borotitanized diffusion layer has a lower hardness as compared to a borided layer. However, contrary results have been reported by Pasechnik et al. [321]. It is further indicated that from all the investigations on holders of heating elements with borided, borochromized, boroaluminized and borotitanized coatings, the maximum wear resistance is observed in borotitanized coatings.

Borotitanizing of commercial iron as well as ZhS6K alloy cannot protect these from high-temperature oxidation [325].

5. BOROZIRCONIZING

Simultaneous diffusion saturation of steel components [illegible] using direct and alternating currents [326, 327]. The following technology of borozirconization has been recommended in [327]: an electrolyte consisting of 95% $Na_2B_4O_7$ + 5% ZrO_2 is contained in a graphite crucible which also acts as the anode during electrolysis. Surface alloying is carried out by electrolyzing at cathodic current density of 0.2 A/cm² for 2 h at 900°C. Using the regime described above, it is possible to produce 130–140 μ thick diffusion layers on medium-carbon steels. The use of an alternating current, under the conditions given below, improves the thickness of the diffusion coating by 30–40%:

$$\tau_r = 1.2\text{–}1.8 \text{ s}, \ t_{an} = 0.4 \text{ s},$$

$$D_{cat} : D_{an} = 0.2 \text{ A/cm}^2 : 0.2 \text{ A/cm}^2 \text{ and } 0.4 \text{ A/cm}^2 : 0.2 \text{ A/cm}^2.$$

An increase in the concentration of zirconium dioxide in the melt is accompanied by a decrease in thickness of the diffusion-coated layer.

Borozirconized coatings do not differ from borided layers in regard to their structure. With the help of x-ray diffraction studies [327] it has been established that zirconium-boride, ZrB_2, and zirconium-carbide, ZrC, phases are also present in the structure along with borides, FeB and Fe_2B. The presence of an intermetallic compound, $ZrFe_2$, in the diffusion layer has also been suggested.

In our view, the constituent phases in the borozirconized coating need to be more specifically defined.

The uses of an alternating current does not influence the phases formed in the layer though it sharply reduces its brittleness (Table 49) [326]. Such an effect of alternating current has been attributed to a more favorable magnitude and character of distribution of the internal stresses in the diffusion layer.

High wear-resistance characteristics of borozirconized coatings are reported by Afanas'ev et al. [326]. Under conditions of static testing, borided steel is better than borozirconized steel. However, contradicting results are

Table 49

Diffusion coating	Maximum brittleness $Z_p = 100$	Rate of change of load, dZ/dp	Brittleness index, $\gamma_p = 100$
Borozirconizing	1.6	0.004	0.64
Borozirconizing using alternating current ($t_r = 1.2$ s)	1.35	0.0035	0.48
Boriding	2.4	0.006	1.44
Boriding using alternating current ($t_r = 1.2$ s)	1.8	0.0056	1.0

obtained, under conditions of dynamic loading. Investigations on wear resistance under conditions of dynamic loading were carried out on a specially modernized MFT-1 machine using bronze (BrOTsS-5-5-5) as the standard (with a maximum load of 100 kg/mm^2 and a sliding velocity of 0.1 m/s, using YSs lubricant along with 10% of abrasive).

Dynamic loading was characterized by the parameter K_d, representing the ratio of maximum and average load.

On increasing K_d from 1 to 2 the wear rate of steel borozirconized by using direct and alternating currents increases by 1.5 times. A figure of similar order was also obtained for steel borided by using an alternating current, whereas in the case of steel borided by using a direct current the wear rate increased by 30 times. Borozirconized steels, as explained in [326], can also withstand higher specific loads without formation of microcracks in the coating as compared to steel borided using the normal standard technology (Table 50) [326].

Table 50

Coating	Dynamic loading, kg/cm^2		
	onset of formation of microcracks	intense formation of microcracks	intense disintegration
Boriding	75	100	125
Borozirconizing	150	200	250
Boriding (using alternating current)	150	200	250

Analysis of the data given in [326] confirms that borozirconized steels do not offer any advantage over steels borided by using an alternating current, as far as wear under dynamic loading is concerned. However, they are slightly better than steels, borided using a direct current, i.e. by using the standard technique. With respect to heat resistance, borozirconized steels are much inferior to borided steels. This conclusion is drawn from a comparison of the results of investigations on the rate of oxidation of borozirconized [327] and borided [328] steel 45.

Intense oxidation of borozirconized specimens begins even at 750°C, whereas in borided specimens, it starts above 850°C. Borozirconized steel has a high corrosion resistance in some active mediums. Thus, as given in [326], borozirconized steels have a higher chemical stability in dilute hydrochloric acid than borided steels (Table 51) [321]. Corrosion in all the specimens was identical.

Table 51

Concentration of hydrochloric acid, wt.%	wt. loss, g/cm^2			
	boriding		borozirconizing	
	10 days	30 days	10 days	30 days
0.05	0.0092	0.0021	0.00045	0.0011
0.1	0.00095	0.0024	0.00047	0.0017
0.2	0.0015	0.0038	0.00058	0.0019
0.5	0.0027	0.0076	0.00074	0.0024
3	0.0063	0.0136	0.0028	0.0087

6. BOROPHOSPHIDING

Presently only one method of simultaneous diffusion saturation of steel with boron and phosphorus is known, namely electrolysis [329]. Melts of $Na_2B_4O_7$–Na_3PO_4 system are used as the electrolyte. Coatings can be obtained only in a fairly narrow concentration range of the melt: 50–70% $Na_2B_4O_7$ + 50–30% Na_3PO_4 (Fig. 78). In melts containing more than 70% $Na_2B_4O_7$, a borided layer is formed and at borax contents below 40% porous phosphided layer is formed (Fe_2P + α-phase).

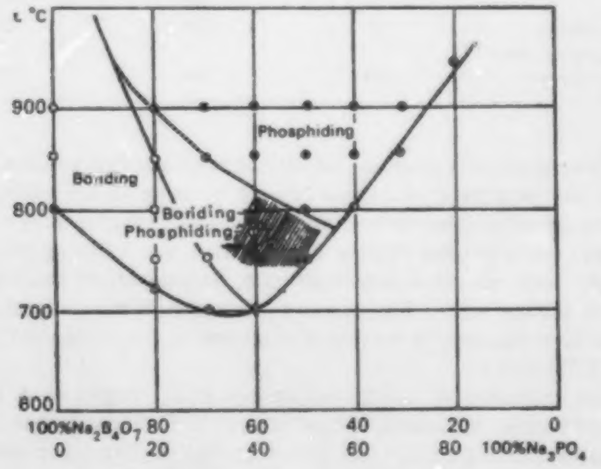

Fig. 78. Variation in thickness of diffusion coating with composition of the melt during electrolytic borophosphiding.

The optimum parameters for electrolysis are temperature—750–800°C and cathodic current density—0.1–0.3 A/cm^2. Dense borophosphiding coatings are formed only in the aforementioned temperature range. Any increase in the treatment temperature gives rise to a porosity in the diffusion-impregnation coating and weakens its bonding with the metal substrate. The impregnation period varies depending on the thickness of the diffusion coating required and is generally between 2–4 h. By impregnating under optimum conditions ($t = 750$–800°C, composition of the melt: 60% $Na_2B_4O_7$ + 40% Na_3PO_4, current density—0.2 A/cm^2, impregnation period 2 h), a dense diffusion-saturated coating about 30 μ thick can be obtained.

At the interface with the borided domain, the borophosphided layer consists of Fe_2B alloyed with phosphorus in addition to which there is the solid solution of boron and phosphorus in α iron. At the interface with the phosphided domain, however, there is Fe_2P alloyed with boron and the α-phase.

In contrast to boriding, a borophosphided coating forms a smooth interface with the metal substrate (Fig. 79).

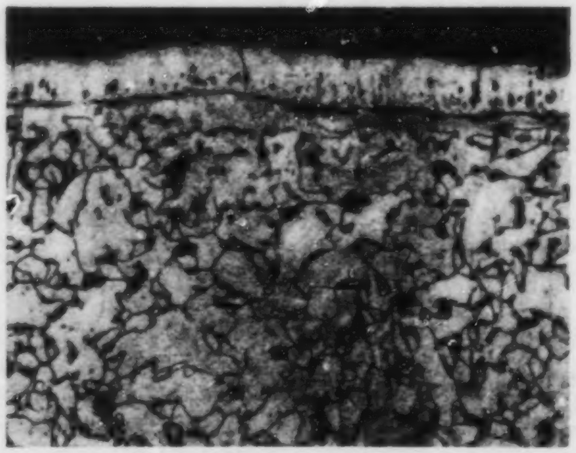

Fig. 79. Microstructure of borophosphided coating.

The effect of the parameters of impregnation on the thickness of a borophosphided coating on Armco iron is shown in Table 52.

Carbon reduces the rate of the diffusion-saturation process. Therefore, borophosphiding of medium- and high-carbon steels involves longer treatment periods ranging from 5 to 7 h.

Table 52

Composition of the melt	Diffusion-saturation regime of Armco iron		Thickness of the borophosphided coating, μ
	t, °C	τ, h	
30% $Na_3PO_4 + 70\%\ Na_2B_4O_7$	800	2	25
	850	2	35
40% $Na_3PO_4 + 60\%\ Na_2B_4O_7$	750	2	20–35
	800	2	28–30
	800	3	52
	850	2	35–37
50% $Na_3PO_4 + 50\%\ Na_2B_4O_7$	750	2	20
	800	2	28
	850	2	40

Table 53

Method of strengthening	Wear, mm^3, in 30 min of testing period
Steel Kh12, hardened and low temperature tempered (HRC 62-63)	1.968
Steel 45, borided (electrolysis using optimum parameters)	0.23
Steel 10, borophosphided	0.23
Steel 10, phosphided	0.92

The wear resistance of borophosphided steels is significantly higher than that of phosphided steels and in no way lower than that of borided steels (Table 53). Wear resistance was measured on a Škoda-Savin machine.

Electrolytic borophosphiding can be used for surface hardening of comparatively weak load carrying parts in machines and instruments (for instance, measuring gages). Additional thermal treatment is not required in this case.

7. SIMULTANEOUS IMPREGNATION OF STEELS WITH BORON AND COPPER

Instead of boriding, simultaneous diffusion saturation of steels with boron and copper, can be employed for surface hardening of machine parts and instruments.

Boriding of steels, alloyed with copper, ensures some reduction in the brittleness of the borided layer [76]. A similar effect can, apparently, be expected in complex alloying of steels with boron and copper.

An impregnating mixture of the following composition was used [276] for simultaneous diffusion saturation of medium carbon steels with boron and copper:

$$92-97.6\%\,(84\%\,B_4C+16\%\,Na_2B_4O_7)+2.4-8\%\,Cu.$$

Surface impregnation was carried out for 6 h at 950°C in containers provided with fusible lids.

In our investigations, aluminothermic mixtures of the following composition were used for simultaneous diffusion saturation of steel with copper and boron:

$$99-97\%\,[80\%\,Al_2O_3+20\%\,(75\%\,B_2O_3+25\%\,Al)]$$
$$+0.5-2.5\%\,CuO+0.5\%\,NaF.$$

The technique of impregnation was similar to that described in [276]. The parameters of treatment were: temperature—1000°C, and duration of the impregnation period—4 h. Any variation in the copper content of the mixture (by introduction of copper or cupric oxide) reduces the thickness of the borided portion of the diffusion coating by a factor of 1/3 or 1/2. At larger concentrations of copper (CuO), impregnation process becomes considerably complicated.

As far as basic mechanical properties are concerned, coatings produced by simultaneous impregnation of steels with boron and copper do not differ much from borided layers (Table 54) [276].

Surface alloying simultaneously with boron and copper is less detrimental to the ductility of steel as compared to boriding [331]. Borided specimens fail in the first cycle of deformation. The addition of small quantities of copper in the impregnating mixture considerably improves the ductility of the diffusion-saturated coating. This is, most probably, not only due to the persence of copper in the diffusion coating, but also due to the reduction of the high-boron phase in it. This is indirectly confirmed from the results of microhardness measurements carried out on specimens simultaneously impregnated with copper and boron. As a result of surface alloying with copper and boron, the microhardness of the diffusion layer on steel 45 decreases from 1800 to 1300–1600 kgf/mm^2. On simultaneous diffusion saturation with copper and boron the fatigue strength of medium carbon steels remains practically unaffected [331].

The diffusion layer produced by simultaneous impregnation with copper and boron is very similar to the borided layer under conditions of sliding friction with lubrication.

Table 54

Coating on steel 45	Parameters of surface hardening		σ	σ_t	δ	ψ	α_H	σ_{-1}	σ^k_{-1}
	t, °C	τ, h	kgf/mm²		%		kg/cm²	kgf/mm²	
Untreated	—	—	61.0	34.0	25.0	52.5	4.5	27.0	5.0
Boriding	950	6	65.0	35.5	13.0	9.0	4.5	30.0	10.0
B–Cu (2% Cu)	950	6	59.5	27.5	20.8	8.2	5.5	26.0	—
B–Cu (4% Cu)	950	6	63.5	32.0	20.5	8.5	5.5	26.0	—
B–Cu (8% Cu)	950	6	65.5	30.0	21.0	9.0	—	26.5	—

Table 55

Composition of mixture, wt.%			Impregnation regime		Wear, mg/cm²
[80% Al_2O_3 + 20% (75% B_2O_3 + 25% Al)]	CuO	NaF	t, °C	τ, h	
99.0	0.5	0.5	1000	4	0.0180
98.5	1.0	0.5	1000	4	0.0140
98.0	1.5	0.5	1000	4	0.0164
97.5	2.0	0.5	1000	4	0.0126
97.0	2.5	0.5	1000	4	0.0316
100	—	—	1000	4	0.0200

Steels diffusion coated simultaneously with boron and copper show some improvement in wear resistance (tests for abrasive wear were carried out using a fixed load of 10 kgf/cm^2 along a path of friction of 10 m) (Table 55). The procedure and equipment used in these investigations were similar to those described by Dauknis [277]. Although the data obtained is promising, this process cannot be recommended for industrial application.

It is necessary to carry out systematic investigations on the kinetics of formation and properties of B–Cu and borided diffusion layers with two phases, and also with a one-phase structure of the borided layer. This type of investigation will enable definite conclusions on the possibility of the practical application of such a process.

While concluding this chapter, it is necessary to note that, on the basis of data available in the literature on the characteristics of complex diffusion coatings (boron being one of the diffusing species) it is not possible to draw any generalized conclusions on the superiority of one or other complex diffusion coating over borided layers. Thus, for example, it has been mentioned earlier that under certain conditions borozirconized steels are observed to have a higher wear resistance than borided steels. This does not, however, necessarily mean that borozirconizing can be recommended, without exception, for all components and surfaces which are subjected to wear.

In order to arrive at such a conclusion, it is necessary to carry out careful comparative studies on the properties of complex and borided diffusion coatings in a wide range of testing parameters (for example, during studies on wear resistance: sliding velocity, magnitude of specific load, parameter K_a, temperature of testing, etc.). We feel that this should be accorded top priority. The significance of such an approach can be illustrated by the following example.

We have carried out investigations on the wear resistance of borided diffusion coatings (including multicomponent systems), in collaboration with Golego, Labunts and Martinayuk. Tests were carried out using the technique described in [330]. A constant load of 10 kgf/mm^2 was used, varying the sliding velocity.

From the data given in Table 56, it can be seen that under the selected conditions of testing, only borozirconized steel 45 has a better wear resistance (at lower sliding rate) than borided steel.

The advantages of other multicomponent diffusion coatings were neither apparent nor discussed. The preference in our recommendation for application will, therefore, be for one-phase borided diffusion coatings (produced in a borax melt with silicon carbide) and not for multicomponent diffusion coating.

From analysis of these results, the following conclusions can be drawn:

1. Results obtained with a set of fixed parameters should not be extended to other conditions, which are beyond the limits of the investigation.

Table 56

Method of hardening steel 45	Impregnation regime		Wear, mg/cm^2·km of sliding rate (dry friction), m/s					
	t, °C	τ, h	0.05	0.1	0.5	1.0	3.0	5.0
Two-phase boriding	1000	2	49	40	8	3.5	2	1
One phase boriding	1020	6	22	12	6	3	2	1
Boroaluminizing*	1000	4	90	60	12	8	3	2
Borosiliconizing (electrolytic)	1000	1.5	47	37	8	3.5	2	1
Borosiliconizing (aluminothermic process)**	1050	6	48	39	9	4.2	2.5	1.5
Borochromizing**	1050	6	50	30	13	9	5	1.5
Borozirconizing**	1050	4	17	12.5	13.4	2.6	1.8	1.3

*The parameters of treatment were selected to give an almost identical (equal to 120–140 μ) thickness of the diffusion-saturated coating.

**The diffusion layer was produced by the aluminothermic process.

(Borozirconized steel has a higher wear resistance than borided steel at low sliding rates whereas opposite results are obtained at higher rates.)

2. Before recommending one or other method of surface hardening for a specific component it is necessary to study all the physicomechanical and chemical factors to which the component is subjected.

3. Our conclusions must be based on the results of investigations and the technoeconomic indexes of other comparable processes.

CHAPTER III

Two-component Coatings Containing Silicon

1. CHROMOSILICONIZING

Simultaneous diffusion saturation of metals and alloys with silicon and chromium—chromosiliconizing—has been known for a fairly long time [332, 333 and others]. Chromosiliconized coatings on low-carbon steels, in certain mediums, have a much better high-temperature oxidation resistance and acid resistance than chromized coatings and a better adhesion than that of siliconized coatings. Chromosiliconizing of iron–carbon alloys improves their resistance to erosion and cavitation. As compared to chromizing, simultaneous impregnation of steels with chromium and silicon hastens the rate of formation of diffusion-saturated coatings.

However, in spite of the fact that chromosiliconized are superior to one-component diffusion coatings in regard to a number of vital physicochemical characteristics, this promising method of surface strengthening has not found wide industrial application.

This can be attributed, most probably, to the nonavailability of adequate technological methods for chromosiliconizing. Till recently, only two methods of chromosiliconizing were tried out: impregnation by the powder method [333–337] (including heating with a high-frequency current [334, 335]) and impregnation using a gaseous phase [283, 332]. Both these methods are laborious and result in low productivity.

Chromosiliconizing using a gaseous phase requires a special and very sophisticated setup.

In recent years, a more promising liquid method for chromosiliconizing has been developed [78, 338].

The aluminothermic process of chromosiliconizing also merits consideration.

Chromosiliconizing in pulverized systems has been studied [335–337 and others].

Impregnation was carried out in hermetically sealed metal containers at 900–1000°C. The treatment duration varied from 3 to 15 h, depending on the thickness of the desired diffusion-coated layer. The mixture used for impregnation consisted of powders of chromium, silicon, aluminum oxide and ammonium chloride [78, 336, 337]. Alternately, a mixture of corresponding ferroalloys can be used [336]. Specially prepared alloys containing 60.2% of Cr and 1.1, 3.55, 5.04 and 8.2% of silicon and the remainder iron, were also used for chromosiliconizing [335, 336]. The alloys were crushed to a size of about 0.5 mm and were blended with chamotte (30% of the weight of the alloy) and ammonium chloride (4% NH_4Cl) powders. The compositions to the impregnating mixtures used in [336] are given in Table 57.

Table 57

Mixture number	Composition of mixture, wt.%			
	Si	Cr	Al_2O_3	NH_4Cl
1	1	55	42	2
2	3	53	42	2
3	5	51	42	2
4	7	49	42	2

An increase in silicon content of the mixture is accompanied by an increase in thickness of the diffusion-saturated coatings (Table 58) [326], but with a decrease in the chromium content.

Table 58

Silicon content of mixture	Thickness of the diffusion layer, μ	
	1000°C	1100°C
1	100	280
3	150	350
5	180	440
7	400	700

In powder mixtures, chromosiliconizing proceeds at a much faster rate when using high-frequency electric heating than while employing normal heating in a furnace [335]. Thus, in the case of diffusion coating of steel 10 and steel 20 in a mixture: (90% CrO + 10% Cu 75) + 30% chamotte powder + 4% NH_4Cl at 1050°C, a 0.2–0.3 mm thick coating was formed within 20 min, as compared to a 0.04–0.05 mm coating formed during normal heating in an electric furnace. The thickness of the diffusion-saturation coating formed on steel U8 under identical conditions was found to be 0.1 mm.

With an increase in the silicon content of the mixture, the impregnation period and temperature, the porosity of the coating also increases. This is true for normal furnace heating as well as for heating with a high-frequency current.

The structural constituents of the diffusion layer obtained by using the processes described above, are given in [336].

In addition to the method of chromosiliconizing in powders of alloys or pure metals, diffusion saturation with chromium and silicon can also be carried out in powders of their oxides, using an aluminothermic method for their reduction.

In order to avoid contamination of the surface layer by aluminum it is necessary to keep its concentration in the mixture well below that required for complete reduction of the oxides. Our investigations in collaboration with Bosenko and Levchenko have shown that the amount of aluminum should not exceed 20% of the weight of the oxides, Cr_2O_3 and SiO_2. The ratio Cr_2O_3/SiO_2 must be of the order of 85/15. Ammonium chloride can act as an activator (1–3%) (Fig. 80). As ane xample, the following composition of the mixture can be recommended for chromosiliconizing:

$$98\%\ \{40\%\ Al_2O_3 + 60\%\ [20\%Al + 80\%\ (85\%Cr_2O_3 + 15\%\ SiO_2)]\} + 2\%NH_4Cl.$$

The concentration of a ballast addition [Al_2O_3] should not be less than 35–40% as, at its lower concentration, considerable heating of the charge takes place, thereby increasing the danger of melting of the surface of the metal substrate.

Increasing the alumina content beyond the suggested range leads to a reduction in thickness of the diffusion layer.

During impregnation in mixtures of the aforementioned composition, an agglomeration of the charge does not take place and the processed specimens are of a silver color without any visible defects.

Formation of layers on all the investigated steels, viz. Armco iron, steel 20, steel 45 and steel U8, begins with α-solid solution. With an increase in the duration of the regime inclusions of precipitate phases appear in the diffusion layer, which may later form a continuous layer. The precipitation of this new phase is favored by a longer treatment period, the lower the temperature the higher the content of carbon in the steel.

Results of x-ray diffraction studies have shown that an ordered solid solution of Fe_3Si, alloyed with chromium is formed on the surface of chromosiliconized (using powder oxides) iron. The microhardness of this solid solution is 850–715 kgf/mm^2. In the superlattice zone, a precipitate of Cr_3Si phase is observed, which is formed during slow cooling from the temperature of impregnation. The zone of solid solutions of chromium and silicon in α-iron with a microhardness of 350–270 kgf/mm^2 lies beyond the superlattice zone.

Under identical conditions of impregnation, solid solutions of chromium

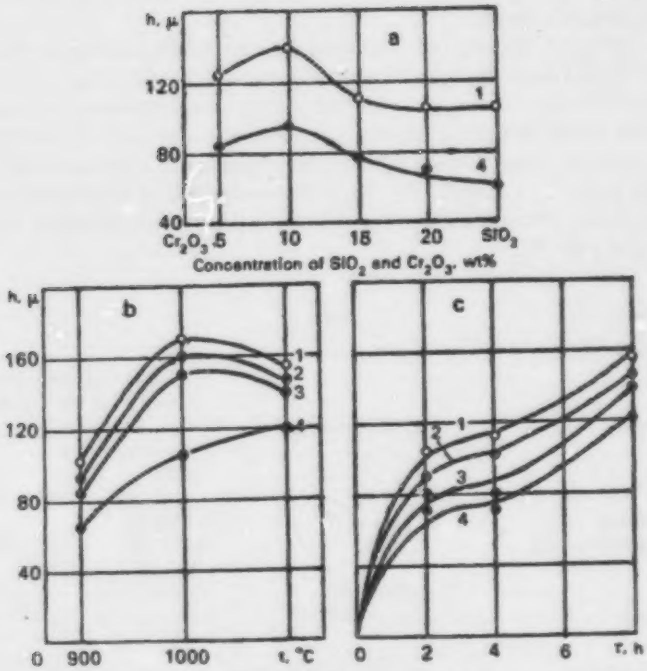

Fig. 80. Effect of parameters of aluminothermic process on chromosiliconizing of steels:

1—Armco iron; 2—steel 20; 3—steel 45; 4—steel U8. Aluminum content in mixture 20%, NH_4Cl—2%:

a—30% Al_2O_3 ($t=1100$°C, $\tau=4$ h); b and c—40% $Al_2O_3+85\%\ Cr_2O_3+15\%\ SiO_2$ (b—$\tau=8$ h, c—$t=1100$°C).

and silicon in α-iron are formed on the surface of steel 45 and steel U8. A layer of carbides $(Cr, Fe)_{23}C_6$ and $(Cr, Fe)_7C_3$ (microhardness 1650 and 1225 kgf/mm^2, respectively) is formed in the middle part of the solid solution. The concentration of chromium at the surface may reach 62.4% and that of silicon, 4.0%.

The microhardness of the α-phase in the zone of carbide inclusions reaches 610–450 kgf/mm^2, whereas in the vicinity of the pearlite zone it is 290–195 kgf/mm^2. Beyond the pearlite zone lies the decarburized zone, in intimate contact with the core.

Gas chromosiliconizing has been thoroughly investigated in [283, 332]; impregnation was carried out at 980°C for 8 h and 24 h: (a) in a hydrogen atmosphere using powders of low-carbon ferrochrome and Si 75 grade ferrosilicon (in a 1 : 1 ratio of the components); (b) in an $HCl+H_2$ medium; (c) in a chlorine atmosphere.

The effect of the method employed for chromosiliconizing on the thickness of the diffusion-saturated layer is shown in Table 59 [293].

On chromosiliconizing in a chlorine atmosphere, a preferred impregnation of steel with silicon takes place irrespective of the ratio of components in the active mixture. Thus, for example, on impregnating in a mixture with a ratio of $FeCr/FeSi = 3 : 1$ at 980°C for 2 h, the concentration of silicon at the surface reaches 6–8%, whereas the concentration of chromium is found to be of the order of 1×10^{-2}%.

Table 59

Treatment	Atmosphere	Thickness of layer, mm, on steel 30 at 980°C after treatment for	
		8 h	24 h
Chromizing	H_2+HCl	0.10–0.14	0.2–0.25
Chromosiliconizing	H_2	0.07–0.10	0.15–0.20
	Cl_2	0.4–0.5	—
	H_2+HCl	0.20–0.25	0.4–0.5

Simultaneous impregnation with silicon and chromium takes place, when chromosiliconizing is carried out in an atmosphere of H_2+HCl. The rate of formation of the diffusion layer, in this case, is lower than that during siliconizing but higher than that in chromizing. The chromium concentration in the surface layer reaches 20% and that of silicon, 5% (treatment parameters temperature 1000°C, duration 2 h, thickness of the diffusion layer obtained 0.25 mm). An increase in the ferrosilicon content in the charge is accompanied by an increase in the thickness of the diffusion layer.

A process of chromosiliconizing in an atmosphere of hydrochloric acid has been developed by Minkevich at the Moscow Institute of Steel and Alloys. In this process, the mixture (ferrochrome + ferrosilicon) and hydrochloric acid are introduced in a retort from one side and the components to be treated are fed in from the opposite side. During impregnation, hydrochloric acid is continuously passed through the retort.

The electrolytic method of chromosiliconizing was developed by Dolmanov and Lyakhovich and was first reported in [78]. A chromosiliconizing bath was prepared by fusing sodium monosilicate with chromic oxide. Sodium chloride was introduced in the melt to increase its fluidity (15–20% of the weight of the mixture).

Lesser quantities of sodium chloride do not have the desired effect and, at higher concentrations, a segregation takes place owing to incomplete dissolution of sodium chloride. Further additions of sodium chloride in quantities well above its solubility in the melt of oxides, $Na_2O+SiO_2+Cr_2O_3$, leads to enhanced rates of evaporation of the salt and consequent atmospheric pollution.

Melts were prepared in the following sequence: sodium silicate was fused, sodium carbonate and quartz sand were then mixed in the required proportions and heated in a gas-fired furnace up to 1400°C and held at this temperature for 3 h.

Sodium monosilicate was fused with sodium chloride. This was followed by the addition of a calculated amount of chromic acid in stages. During these additions, the bath was carefully stirred.

By varying the ratio of the constituents of the bath (Na_2SiO_3 and Cr_2O_3), the parameters of electrolysis and temperature of the impregnation process, it is possible to control the amount of active atoms of chromium and silicon (in a fairly wide range) and thus, modify the structure of the layer (from pure siliconizing through chromosiliconizing to pure chromizing) and, consequently, its properties.

The characteristics of diffusion layers on steel 45, produced under varying conditions of impregnation, modes of electrolysis and temperatures of the process are shown in Fig. 20 (1100°C—solid line, 1000°C—dashed line). This figure consists of four zones. In the first zone a diffusion layer does not form, as the current density employed is not sufficient for the formation of active atoms of silicon and chromium. In the second zone a preferred deposition of chromium atoms takes place at the cathode, resulting in the formation of a typical chromized coating on the surface of the steel (Fig. 81). In the fourth

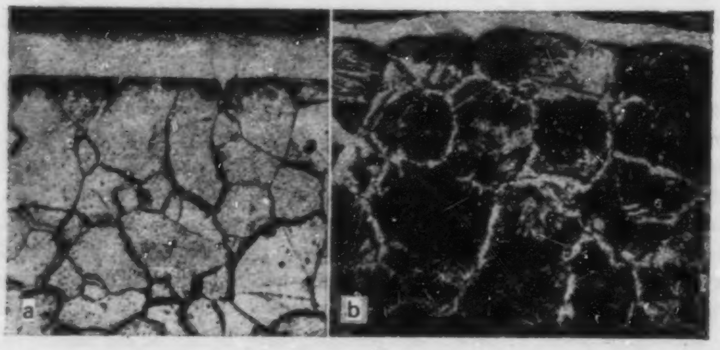

Fig. 81. Microstructures of chromosiliconized layers (electrolytic process, 15–20% Cr_2O_3, $t=1100$°C, $\tau=3$ h, ×240):
a—Armco iron; b—steel 45.

zone a preferred deposition of silicon atoms takes place at the cathode thus producing a diffusion layer similar to a siliconized coating (α-solid solution with a microhardness of 300–500 kgf/mm^2, Fig. 82). In the third zone, multicomponent diffusion saturation of steel with chromium and silicon takes place. The diffusion layer has a structure 'in between' those described above: on the surface, a carbide layer is formed and beneath it exists a zone of α-solid solution (Fig. 83, a). Chromosiliconized layers on Armco iron and carbon steels consist of solid solutions of silicon and chromium in α-iron (Fig. 83, b).

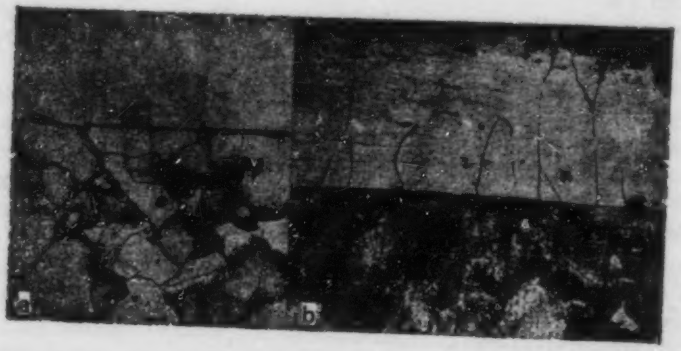

Fig. 82. Microstructure of chromosiliconized layers (electrolytic process, 0–5% Cr_2O_3, $t = 1100$°C, $\tau = 3$ h):

a—Armco iron (×240); b—steel 45 (×320).

From the plot of phases formed during impregnation, it can be seen that chromosiliconizing takes place in all melts which contain not less than 5% of chromic oxide and at current densities higher than 0.15 A/cm^2. An increase in the quantity of chromic oxide in the melt broadens the zone of chromosiliconizing. In order to establish optimum parameters for chromosiliconizing, investigations were made on the effect of the mode of electrolysis and composition of the melt on the thickness, structure and chemical composition of the diffusion layer. From the data given in Fig. 84, it can be seen that it is unnecessary to increase the current density beyond 0.3 A/cm^2, as this does not bring about any significant increase in the thickness of the chromosiliconized layer. All further investigations were, therefore, carried out at a current density 0.3 A/cm^2.

The composition of the electrolyte can greatly influence the thickness and chemical composition of the diffusion layer. On increasing the chromic-oxide concentration in the melt, the thickness of the diffusion layer decreases, but the concentration of chromium in it is increased.

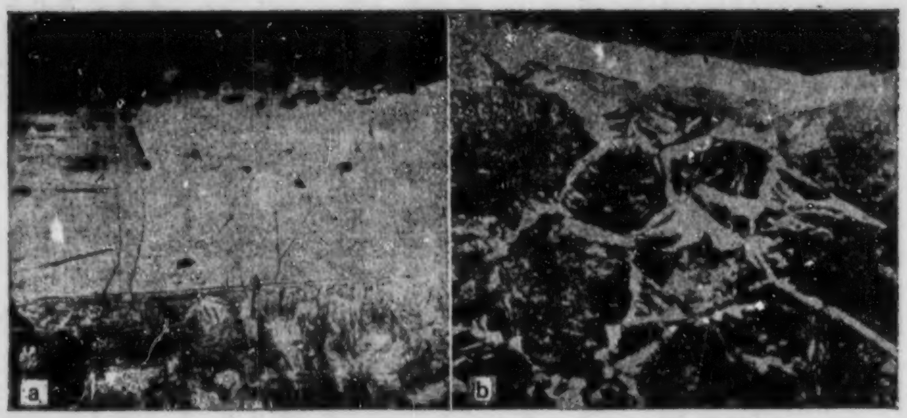

Fig. 83. Microstructure of chromosiliconized layers (electrolytic process, 10–15% Cr_2O_3, $t = 1100°C$, $\tau = 3$ h, ×240):

a—Armco iron; b—steel 45.

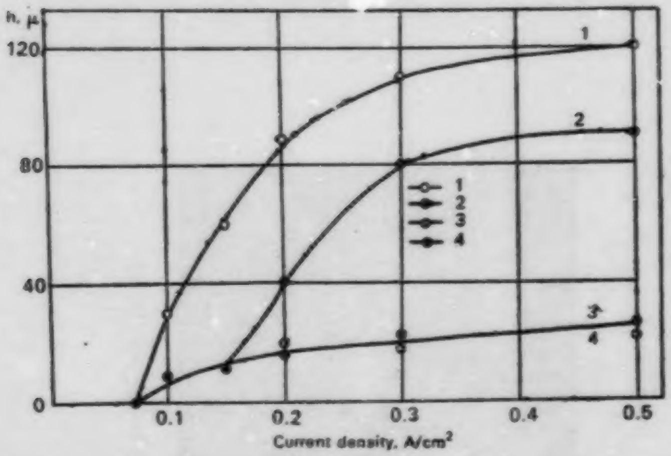

Fig. 84. Effect of current density on thickness of chromosiliconzied layer (15% Cr_2O_3, $t=1100°C$, $\tau=3$ h):

1—Armco iron; 2—steel 20; 3—steel 45; 4—steel U8.

Analysis was carried out with an ISP-28 spectrograph using copper electrodes with a duration of burning of 10 s followed by an exposure of 35 s in the spark-excitation mode. The depth of the surface penetrated did not exceed 3–5 μ.

In [133], the following composition of the melt is recommended as optimum for chromosiliconizing.

Sodium silicate (Na_2SiO_3)	65–70%
Chromic oxide (Cr_2O_3)	10–15%
Sodium chloride (NaCl)	20%

It is further recommended that impregnation should be carried out at 1000–1100°C. At temperatures below 1000°C there is a sharp decline in the solubility of sodium chloride in the Na_2SiO_3–Cr_2O_3 system, which consequently increases the viscosity of the melt. The upper limit of the temperature interval is determined by technical considerations (pitting of the crucible, reduction in the strength of the crucible, suspension system, reduction in the life of the heating element, etc.). The duration of impregnation regime generally varies between 4 to 6 h.

Under optimum conditions of impregnation ($t=1050$–$1100°C$, $\tau=5$ h, composition of the mixture 15% Cr_2O_3 + 75% Na_2SiO_3 + 10% NaCl) the concentrations of chromium and silicon in the diffusion layer on Armco iron (α-phase) reach 40–50% and 8–10%, respectively [133].

According to spectral analysis, the carbide layer formed on chromosiliconized carbon steels contains about 2.8–3% of silicon. X-ray diffraction studies have shown that silicide phases are not formed in the diffusion layer on carbon steels when these coatings are produced by electrolytic chromosiliconizing. It is, therefore, necessary to assume that silicon is soluble in the carbide, $Cr_{23}C_6$. No appreciable change in the silicon content of the diffusion saturation layer was observed when the Cr_2O_3 concentration in the melt was reduced from 20% to 15% and the temperature was increased from 1000 to 1100°C.

Electroless liquid-phase chromosiliconizing is carried out in baths of the same composition but with the addition of specified amounts of the corresponding reducing agents. For this purpose calcium silicide can be used. It is cheap, easily available and can be easily ground to the required size. Calcium silicide is introduced in the melt in the form of granules of the size 0.32–1.6 mm. The additions vary between 10–12% of the weight of the melt. On reducing the concentration of calcium silicide in the melt the rate of formation as well as the uniformity of the coating are affected. On the other hand, the use of larger quantities of calcium silicide leads to an increase in the viscosity of the melt. As a rule, the size of the granules should increase with an increase in the treatment temperature. Thus, the following sizes should be used for various temperature intervals:

1000°C	0.32–0.63 mm
1000–1050°C	0.5–1.0 mm
1050–1100°C	1.0–1.6 mm

This is based on observations of the authors and needs experimental confirmation. Data on the effect of the composition of the melt on the thickness of the diffusion layer produced by electroless liquid chromosiliconizing is given in Table 60 [323]. Comparative data on electrolytic chromosiliconizing has also been given in the same Table. As far as the rate of formation of the diffusion saturation layer is concerned, electroless liquid-phase and electrolytic methods of chromosiliconizing are not very different from each other. Studies in the structure and structural constituents of the diffusion layer produced by electroless and electrolytic chromizing have established an almost complete similarity between them (Fig. 85). For industrial application the use of melts containing 15% of Cr_2O_3 is recommended.

Based on considerations of cost, the electroless method of chromosiliconizing is on a par with the earlier described methods. The technological advantages of this method vis-a-vis the gas-phase and electrolytic processes are obvious.

The effect of the temperature of impregnation regime ($\tau = 10$ h) on the thickness of chromosiliconized coatings on Armco iron produced in a powder mixture of chromium, silicon, alumina and ammonium chloride is discussed

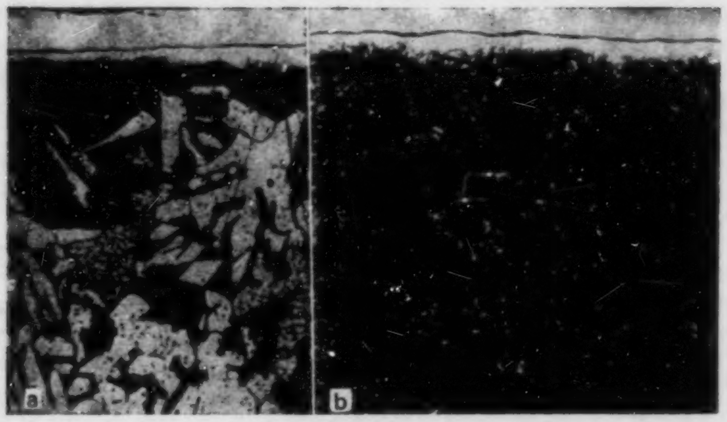

Fig. 85. Microstructures of chromosiliconized coatings:
a—steel 45, electrolytic process (15% Cr_2O_3, $t = 1100°C$, $\tau = 3$ h); b—steel ShKh15, electroless process with reduction of Na_2SiO_3 and Cr_2O_3 by calcium silicide.

Table 60

Composition of melt, %			Thickness of layer, in μ, on steel 45 processed at 1100°C for 4 h	
Cr_2O_3	Na_2SiO_3	NaCl	electrolytic process	electroless process, calcium silicide 10%
0–5	90–85	10	200–180	190–160
5–10	85–80	10	180–100	160–80
10–15	80–75	10	100–50	80–40
15–20	75–70	10	50–30	40–30

in [336]. Gas chromosiliconizing of steel 30 was carried out at 1000°C for 8 and 24 h [283]. This data is so limited that it is inadequate to assess the effect of the parameters on the kinetics of formation of diffusion layers produced from powder mixtures of metals or ferroalloys or by gaseous phases, and to make a comparison between these methods of chromosiliconizing and the electrolytic and electroless liquid chromosiliconizing processes. We shall, therefore, restrict our discussion to only those results which are obtained for chromosiliconizing in fused baths and powder oxides.

The rate of formation of a diffusion layer (produced by electrolytic chromosiliconization) on Armco iron, steel 20, steel 45 and steel U8 at 1000, 1050 and 1100°C has been studied [78]. The duration of impregnation regime varied from 1 to 5 h. Chromosiliconizing was carried out in melts of the following compositions at a current density of 0.3 A/cm^2:

$$(90\%\ Na_2SiO_3 + 10\%\ Cr_2O_3) + 10\text{–}20\%\ NaCl,$$

$$(85\%\ Na_2SiO_3 + 15\%\ Cr_2O_3) + 10\text{–}20\%\ NaCl.$$

The results given in Figs. 86–88 indicate a complex mechanism of formation of a chromosiliconized layer as compared to one-component diffusion coatings.

During impregnation in mixtures containing 15% of Cr_2O_3, it has been observed that there is a monotonic increase in the thickness of the diffusion layer with an increase in temperature and duration of treatment. However, the temperature dependence of the thickness of a diffusion layer is certainly not of an exponential type (Fig. 86).

During chromosiliconizing in a mixture containing 10% of Cr_2O_3, in the temperature range of 1000–1050°C, it has been observed that the thickness of the diffusion layer either passes across a maximum or shows such a tendency (depending on the duration of the process). First, it rises with temperature

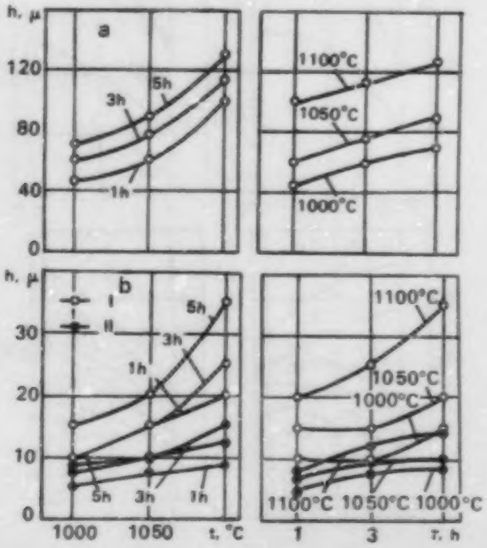

Fig. 86. Variation in thickness of a diffusion layer with temperature and duration of chromosiliconzing process (15% Cr_2O_3):

a—Armco iron: b—(I) steel 45 and (II) steel U8.

and then starts falling at higher temperatures (Fig. 87). A similar temperature dependence has been observed during impregnation in powder oxides (Fig. 88). The authors of [336] associate the observed pattern of change in the thickness of the diffusion layer with a change in the rates of diffusion elements, when an increase in temperature leads to an increase in the amount of diffusing chromium which possesses a slower rate of diffusion. The slow rate of diffusion of chromium as compared to that of silicon consequently leads to a reduction in the thickness of the diffusion-saturated coating. An increase in the concentration of chromium under similar conditions should lead to a slowing down of the rate of growth of the diffusion layer, albeit, for different reasons: chromium reduces, the solubility of silicon in α-phase and this, subsequently, results in a sharp decrease in the coefficient of diffusion of silicon. According to the data of Fitzer [339], a reduction in the concentration of silicon from the maximum to the minimum limit results in a fall in the coefficient of diffusion of silicon in α-phase by a factor of 20.

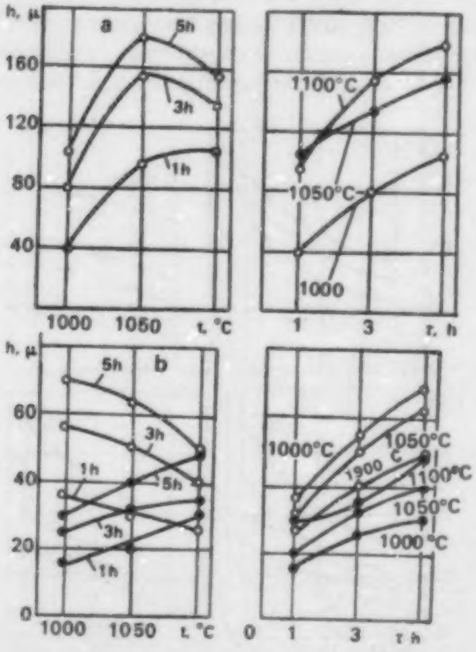

Fig. 87. Effect of temperature and duration of chromosiliconizing process (10% Cr_2O_3) on thickness of a diffusion-saturated layer:

a—Armco iron; b—(I) steel 45 and (II) steel U8.

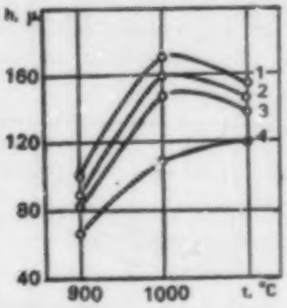

Fig. 88. Effect of temperature during impregnation on thickness of diffusion layer produced by chromosiliconizing (aluminothermic method) ($\tau=8$ h):

1—Armco iron; 2—steel 20; 3—steel 45; 4—steel U8. Composition of mixture: 98% {40% Al_2O_3 + 60% [20% Al + 80% (85% Cr_2O_3 + 15% SiO_2)]} + 2% NH_4Cl.

However, such an approach to explain the temperature dependence of the growth of a chromosiliconized layer appears to be oversimplified. On increasing the temperature during chromosiliconizing in a bath containing 15% of Cr_2O_3, there is a similar increase in absolute concentration of the element with a slower rate of diffusion, i.e. chromium, and yet there is a monotonic rise in the thickness of the diffusion layer with increasing temperature.

The thickness of a chromosiliconized layer (from the surface to the limit where there is a phase change) is determined by the rate of diffusion of chromium and silicon in α-phase and the absolute values and ratio of concentrations of these elements in the diffusion layer. On changing the temperature:

1. there is a variation in the limiting concentrations of chromium and silicon at which a narrowing of the γ-zone takes place. Further, this change, starting from the binary systems Fe–Cr and Fe–Si, takes place due to a very complex mechanism which varies with the ratio of chromium and silicon;
2. there is a variation in the diffusion coefficients, the nature of which is different for chromium and silicon;
3. there is a variation in the rate of formation of active atoms of chromium and silicon, as well as in the rate of their transfer to the substrate surface; and
4. there is a variation in absolute values of concentrations and proportions of the diffusing atoms of chromium and silicon; this itself leads to changes in the limiting concentrations responsible for phase transformation, as well as variations in the rates of diffusion of both the elements.

Without conducting specific investigations, it is not possible to analyze the effect of the various factors, listed above, on the thickness of chromosiliconized layers.

The temperature dependence of the growth of a chromosiliconized layer produced by electroless liquid chromosiliconizing (in melts containing 10% of Cr_2O_3) (Fig 89) and by diffusion saturation in powder metals has not been verified.

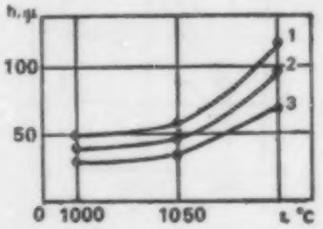

Fig. 89. Effect of parameters of saturation on thickness of chromosiliconized layer on Armco iron:

1—2 h; 2—4 h; 3—6 h.

The structural constituents of the diffusion layer were studied with the help of metallographic and x-ray structural analysis. The diffusion layer on Armco iron, obtained with various parameters consisted of α-solid solution of chromium and silicon in iron.

The structure of diffusion layers on steels depends on the parameters of impregnation regime. In chromosiliconizing in melts containing 15% of Cr_2O_3, the different phases formed in the diffusion layer on steel 45 and steel U8 are distributed in the following order from the surface to the volume: $Cr_{23}C_6 \rightarrow Cr_7C_3 \rightarrow$ α-solid solution. On varying the temperature of the chromosiliconizing process only the proportions of these phases are changed. The diffusion layer on steel 20, steel 45 and steel U8, produced at 1000°C in a melt containing 10% of Cr_2O_3, consists of α-phase with a small quantity of carbide phase, $Cr_{23}C_6$. At 1100°C the structure of the diffusion layer is identical to that described above for a melt containing 15% of Cr_2O_3.

From the data given above (see Figs. 86 and 87), it is possible to evaluate the effect of carbon on the thickness of a chromosiliconized layer. During surface impregnation in melts containing 15% of Cr_2O_3, with concentrations of carbon up to 0.4%, there is a sharp reduction in the thickness of the chromosiliconized layer. Further increases in carbon concentration have a marginal effect on the thickness of the diffusion layer (Fig. 90, b). Such a variation in the thickness of a diffusion layer is related to its structure. On steels containing more than 0.2% of carbon, the principal structural constituent of the layer is the carbide zone and the zone of α-solid solution is not broad. With increase in carbon content of the metal, the formation of carbide zone is facilitated resulting in a marginal improvement in its thickness.

The larger thickness of diffusion layers on steel 20 as compared to those on steel 45 and steel U8 is due to a better-developed α-solid solution zone in the

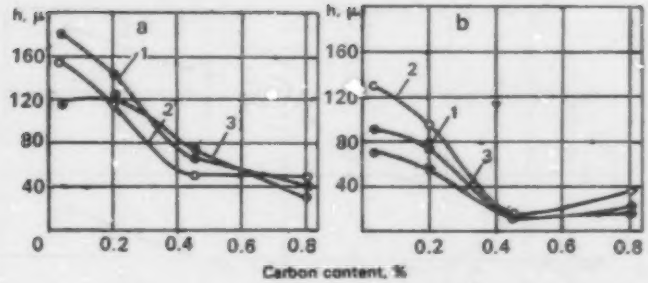

Fig. 90. Effect of carbon concentration in steel on thickness of chromosiliconized layer:

a—melt containing 10% Cr_2O_3; b—melt containing 15% Cr_2O_3.
1—1050°C; 2—1100°C; 3—1000°C.

former. During chromosiliconizing in melts containing 10% of Cr_2O_3, a gradual decrease in the thickness of the diffusion layer with increasing carbon concentration in the steel is observed. In this case, the amount of active atoms of chromium formed is considerably low (due to the low concentration of Cr_2O_3—only 10%) and insufficient for the formation of a carbide layer of significant thickness and, hence, the contribution of the carbide zone toward the overall thickness of the diffusion impregnation layer is not much. Its thickness remains practically unchanged irrespective of the carbon content in the steel.

The results obtained were checked on carburized specimens of Armco iron in accordance with the experimental procedure described by Voroshnin and Lyakhovich [340]. Chromosiliconizing was carried out for 3 h at 1100°C in a melt containing 15% of Cr_2O_3. The results of these investigations are given in Fig. 91. These substantiate the earlier drawn conclusions.

Some of the mechanisms of structure formation during chromosiliconizing of steels could be better understood by using highly sophisticated methods for investigating the effect of carbon on the thickness of diffusion-saturated coatings. The thickness of the α-phase sharply decreases in the concentration interval of 0.05–0.2% C; beyond this range no further change is observed. The formation of carbide phase begins even at 0.07–0.08% C. A further increase in the carbon content up to 0.2% leads to an increase in thickness and continuity of the carbide zone. The thickness of the carbide zone remains practically unchanged for carbon concentrations of between 0.3 to 0.8%. Any further increase in carbon content is accompanied by a reduction in the thickness of the carbide zone.

The microhardness of the carbide zone increases from 1360 kg/mm^2 at 0.2% C to 1700 kg/mm^2 at 1% C. The appearance of the bend in the curve, in

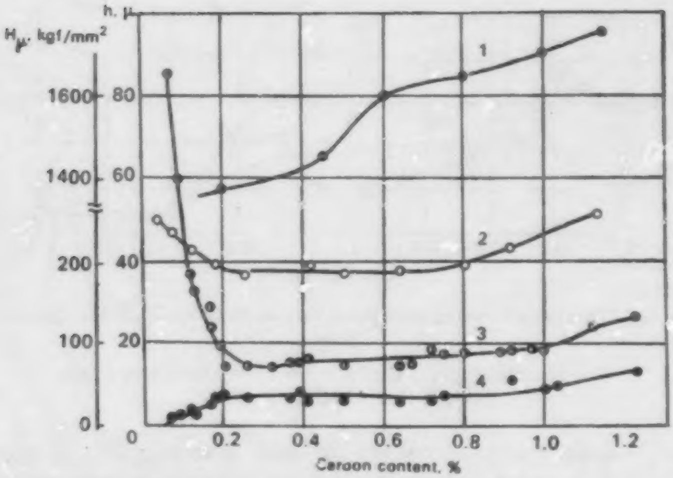

Fig. 91. Effect of carbon concentration in steel on depth, structure and microhardness of constituent phases in a chromosiliconized layer:

1 and 2—microhardness of carbide and α-solid solution layer respectively; 3 and 4—thickness of carbide and α-solid solution zones, respectively (Cr_2O_3—15%, $t = 1100°C$).

the carbon concentration range of 0.4–0.6% C, can possibly be attributed to the formation of a second carbide phase. This is supported by the results of investigations on the effect of carbon concentration in regard to the development of structures during diffusion chromizing [101, 341]. During chromizing of low-carbon (0.15–0.25% C) steels, a carbide layer is formed on the surface, consisting of one of the carbide phases—(Cr, Fe)$_7$C$_3$ or (Cr, Fe)$_{23}$C$_6$—depending on the parameters of impregnation. In chromizing of steels containing 0.41–1.0% of carbon, the diffusion coating consists of carbide phases—(Cr, Fe)$_{23}$C$_6$ and (Cr, Fe)$_7$C$_3$. The microhardness of the α-phases decreases in the carbon concentration range of 0.05 to 0.2%, and somewhat increases when the carbon concentration is higher than 0.8%. In the concentration range of 0.2–0.8% of carbon, there is no appreciable change in the microhardness of the α-phase and it remains at between 190–200 kgf/mm².

Depending on the method and treatment parameters, the concentration of carbon and alloying elements, chromosiliconizing can result in diffusion coatings with different structures and constituent phases with varying ratios of the chromium and silicon contents and with different complex physicochemical properties.

Electrolytic and electroless liquid chromosiliconizing of Armco iron and low-carbon steels (containing up to 0.15% C) result in diffusion layers which consists of α-solid solution of chromium and silicon in iron. The surface hardness of such coatings is found to be 260–270 kgf/mm². The variation in microhardness of the chromosiliconized layer in its depth is shown in Fig. 92.

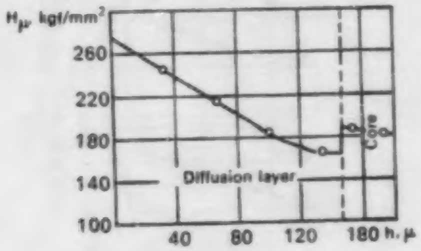

Fig. 92. Variation of microhardness of chromosiliconized layer in its depth: Bath contained 15% Cr_2O_3, $t = 1100°C$, $\tau = 4$ h.

The diffusion layer obtained on Armco iron by chromosiliconizing in powder mixtures containing silicon, chromium, along with alumina and ammonium-chloride additions, consisted of two zones: an outer zone with a porous layer and a microhardness of between 440–300 kgf/mm² and an internal zone consisting of a dense mass with a microhardness of 280–160 kgf/mm² [336].

The diffusion layer, formed on the surface of steels, with a carbon content higher than 0.15%, consists of carbides of chromium ($Cr_{23}C_6$ and Cr_7C_3) and α-phase. The hardness of the carbide layer was found to be between 1400–1700 kgf/mm². The surface hardness of the diffusion coating increases with an increase in the carbon content of the steel (Fig. 93). As carbides of chromium and other transition elements have a very narrow range of composition, the improvement in hardness, resulting from an increase in the carbon content of the steel, cannot be attributed to a change in chemical composition of the carbide, $Cr_{23}C_6$. It could possibly be related to the increase in thickness of the diffusion layer, and to the absolute and relative amounts of the phases in it.

During diffusion coating of steels, in melts containing 10% of Cr_2O_3 at 1000°C for 3 h, the layer formed consists of α-solid solution owing to an insufficiency of active atoms of chromium for formation of carbides and its microhardness varies from 250 to 450 kgf/mm².

Chromosiliconized coatings on Armco iron and low-carbon steels can be subjected to artificial aging.

Chromosiliconized layers on steels ensure an improved wear resistance. The effect of various technological parameters of the process of chromosiliconizing in powder mixtures on the wear resistance of steel 45 and steel U8 have been investigated by employing systematically planned experiments.

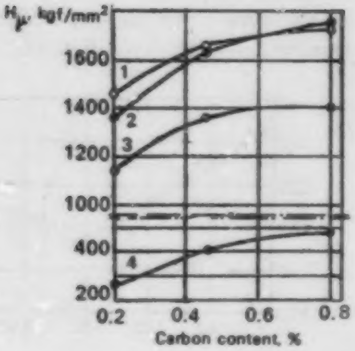

Fig. 93. Effect of carbon concentration in steel on microhardness of chromosiliconized coatings:

1—bath containing 15% Cr_2O_3, $t=1100°C$; 2—bath containing 10% Cr_2O_3, $t=1100°C$; 3—bath containing 15% Cr_2O_3, $t=1000°C$; and 4—bath containing 10% Cr_2O_3, $t=1000°C$.

Chromosiliconizing was carried out in a powder mixture of silicon, ferrochrome (grade—Kh75), aluminum oxide and ammonium chloride. Tests on wear resistance were conducted on a Shkoda Savin-type machine under the following experimental conditions:

1. rate of rotation of hard-alloy disk ($d=62.5$ mm, $h=2.4$ mm, HRC 74-75)—860 rpm;
2. load—2.1 kg; and
3. total testing period—30 min.

The extent of wear was estimated by the volume of the metal removed measured in mm³.

On chromosiliconizing of steel 45 and steel U8 under optimum conditions: $t=1000°C$, $\tau=6$–7 h, composition of the mixture—2.5% Si+55–60% Cr 75+42.0–37% Al_2O_3+0.5% NH_4Cl (without subsequent heat treatment) their wear resistance increased by 2.1 to 8.1 times respectively as compared to their hardened and low-temperature tempered state. As compared to chromizing the improvement was from 10–15%.

Chromosiliconized layers on low-carbon steels have a much higher ductility than siliconized layers [283]. The high heat resistance of chromosiliconized steels has been widely reported on in the literature [78, 101, 283, 284, 332, 335, 338]. Low-carbon steels chromosiliconized using a gaseous phase are known to have a better heat resistance than that obtained by chromizing or siliconizing [283, 332].

According to the data given in [283, 332], different types of diffusion coatings were damaged, to some extent, by the attack of furnace gases at the temperatures given below:

Type of treatment	Temperature, °C
Chromizing	800
Siliconizing	900
Chromosiliconizing	1000
Chromoaluminizing	1050
Aluminizing	1150

Comparative data on the heat resistance of stainless steels, chromized Armco iron, electrolytically chromosiliconized Armco iron and steel 20 at 900°C is given in Fig. 94. Chromizing was carried out in a powder mixture containing 50% of Cr+47% of Al_2O_3+3% of NH_4Cl at 1000°C for 24 h: chromosiliconizing from a melt with 15% Cr_2O_3 at 1100°C for 4 h. The heat resistance of chromosiliconized steel was found to be similar to that of chromized specimens. The difference between the heat resistance of chromized and chromosiliconized steels increases with a rise in temperature (in the temperature range of 700–900°C). The high heat resistance of chromosiliconized steels is attributed to the formation of a dense surface layer: $(Cr, Fe)_2O_3$ or $FeO \cdot Cr_2O_3$ and SiO_2. It is possible that a complex layer (consisting of spinel type $FeO \cdot Cr_2O_3 \cdot SiO_2$) are formed. These layers are known to have highly protective quality.

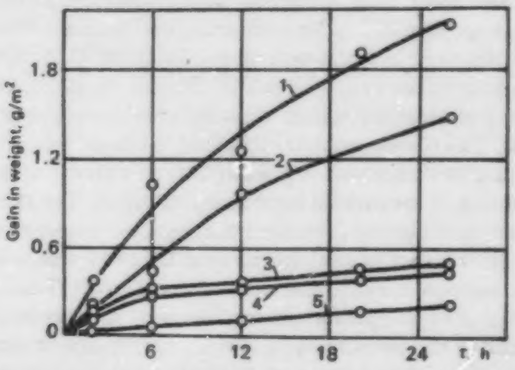

Fig. 94. Heat resistance of chromized and chromosiliconized layers:

1—chromized Armco iron; 2—chromized steel 45; 3—chromosiliconized steel 45; 4—chromosiliconized Armco iron; 5—steel Kh18N9T; t=900°C.

The effect of the parameters of impregnation on the heat resistance of steels has been investigated for two methods: solid-phase [338] and liquid-phase.

The heat-resistant characteristics of plain carbon steels (08KP steel, steel 45) are very strongly dependent on the duration of treatment, the temperature of the process, the concentration of ammonium chloride and silicon in the mixture and also, though to a much lesser extent, on the ferrochromium content in the active mixture [338].

The kinetics of oxidation of chromized and chromosiliconized (according to optimum regime [338]) plain carbon steels have been investigated at 800, 900 and 1000°C. The kinetics of oxidation of chromized steels at all temperatures of investigation generally follows a parabolic law. The kinetics of oxidation of steel 45 and steel U8 with diffusion-saturated chromosiliconized coatings is also of a parabolic type. The parabolic law of oxidation of chromosiliconized steel 08KP is observed only at relatively low temperatures of oxidation (800°C). In the temperature interval of 800–900°C the rates of oxidation of chromized and chromosiliconized steel 45 and steel U8 are about the same. At 1000°C the heat resistance of chromized steels is higher than that of chromosiliconized steels. At 800°C, chromosiliconized steel 08KP has a superior oxidation resistance than that of chromized steel. However, at higher temperature (900–1000°C), oxidation resistance of the latter is much higher. The observation that the resistance of all carbide diffusion coatings at all temperatures of investigations is higher than that of α-phase, is in agreement with the data of Dubinin [101].

Chromized coatings on all the investigated steels had a high thermal stability: on steel 08KP they withstood all the investigated thermal-cycling regimes up to more than 200 cycles without failure. On steel 45 also, the coat[illegible] withstood 200 thermal cycles without failure at 800°C. At 900 and 1000°C the corresponding values were 100 and 60 thermal cycles, respectively. The thermal stability of carbide coatings increases with the rise in carbon concentration in steel. This phenomenon is attributed to the reduction in the volume effect of γ–α transformation with increasing carbon concentration in steel and a better uniformity of the carbide layer along its depth. The thermal stability of diffusion-saturated chromosiliconized coatings, as compared to chromized coatings, is slightly higher in steel 45 and steel U8 and lower in steel 08KP.

Attempt to improve the heat resistance of steel Kh18N9T and steel Kh25T, by chromosiliconizing in a pulverized medium were unsuccessful.

On the basis of the investigations carried out, it can be confirmed that, with respect to oxidation resistance, chromized and chromosiliconized carbon steels are almost as good as special types of stainless steels (Kh18N9T and Kh25T). Chromizing and chromosiliconizing (in powders of ferroalloys) should be considered as equivalent processes for improving the heat resistance of carbon steels. Chromosiliconized diffusion coatings do not offer any specific advantage over chromized coatings.

Chromosiliconized steels have a high corrosion resistance in various aggressive mediums.

Gas chromosiliconized steel 30 is in no way inferior to chromized steel as far as corrosion resistance in sea water is concerned [283].

Comparative data on the acid resistance of stainless steel Kh18N9T and Armco iron and steel 20, chromosiliconized by an electrolytic method, in 10% dilute acids is given in Table 61 [78]. The testing period was 200 h. Steel Kh18N9T was taken as the standard (100%) for purposes of comparison. The maximum stability close to that of stainless steel Kh18N9T, is that of a chromosiliconized layer in dilute nitric acid. In sulfuric and hydrochloric acids chromosiliconized layers reveal a fairly high stability but considerably lower than that of steel Kh18N9T. In all the investigated mediums, chromosiliconized steels exhibited a much higher acid resistance than chromized steels (the treatment parameters were the same, as in investigations on heat resistance).

Table 61

Testing medium	Stability, %				
	Kh18N9T	steel 20	chromized commercial iron	chromosiliconized steel 20	chromosiliconized commercial iron
10% H_2SO_4	100	0	1.9	3.0	15
10% HCl	100	0	6.3	17.0	23
10% HNO_3	100	0	4.4	50.0	73

The resistance of chromosiliconized steel 45 to acid corrosion, in the investigated mediums, was lower than that of Armco iron, due to lack of continuity in the carbide layer. Studies on the condition of the surface of the specimen and metallographic analysis after the test established the presence of a pin-hole porosity on the surface of steel, through which the aggressive mediums attack the substrate metal and facilitate corrosion. There is a basis for presuming that a chromosiliconized layer (carbide) on high-carbon steels would exhibit a significantly higher corrosion resistance than that on medium-carbon steels. No traces of corrosion damage were observed on chromosiliconized (by electrolytic method) low-carbon steels, when tested in 10% dilute solutions of sodium chloride and sodium hydroxide for 300 h.

Similar results were obtained for chromosiliconized layers produced by electroless liquid and aluminothermic processes (Table 62). Chromosiliconizing improves the erosion resistance of the surface in a high-temperature gaseous medium [101].

The combination of high hardness of chromosiliconized medium and high-carbon steels together with their improved oxidation and corrosion resistance leads us to recommend this method of surface strengthening for

Table 62

Testing medium	Weight loss in 100 h of testing, mg/cm^2				
	Armco iron		Cermet PZhZM, densification, 85%		
	untreated	chromo-siliconized	untreated	chromosiliconized	carburized and chromosiliconized
10% NaOH	0.7	0.1	3.1	0.5	3.0
5% NaCl	0.9	0.6	3.5	1.1	0.8

Remarks: Stability of cermet in acid solutions is not improved by chromosiliconizing.

improvement of surfaces and machine parts exposed to complex conditions such as: erosion at elevated temperatures, in corrosive mediums, etc. Tools used for hot forging are a good example of components exposed to such conditions.

2. MOLYBDENOSILICONIZING

Methods of molybdenosiliconizing have been developed. These are the electrolytic and electroless liquid methods.

The electrolytic method of molybdenosiliconizing has been described in [342]. Diffusion coating was carried out in melts of Na_2SiO_3–Na_2MoO_4 system at 1000–1100°C. The upper value of the temperature interval is limited by the technological parameters and the lower limit is controlled by the sharp decrease in the solubility of sodium monosilicate in Na_2MoO_4 with a fall in the regime temperature. The current density during impregnation was maintained at 0.15–0.2 A/cm^2. A reduction in current density during electrolysis leads to a decrease in the rate of impregnation, whereas there is no change in results if the current density is increased beyond the range specified above.

The maximum rate of the process is observed when the concentration of sodium monosilicate in the melt is approximately 50–60 mol%. At higher or lower concentrations of Na_2SiO_3, a slight reduction in the thickness of the diffusion layer is observed. A sharp reduction in the rate of formation of the diffusion layer is observed at an Na_2MoO_4 concentration of about 5 mol% (see Fig. 1). The authors of [342] have attributed this to the formation of silicides of molybdenum in the melt which is deposited at the cathode in the form of a loosely held porous mass.

In the wide concentration interval of sodium molybdate ranging from 100 to 20 mol%, it is mainly molybdenum that is deposited at the cathode. This is confirmed by the formation of a thin carbide layer on the surface of steel 45. When the concentration of Na_2MoO_4 in the bath is less than 5 mol%, there is a preferred deposition of silicon at the cathode resulting in the formation of siliconized layers, consisting of acicular grains of α-solid solution, on the surface of iron as well as steels. It is well known that in alloys of the Fe–Si system, molybdenum suppresses the formation of α'-phase. From this point of view, the need for more detailed investigations, on the effect of small additions of Na_2MoO_4 to sodium monosilicate on the surface of the siliconized diffusion layer produced by the electrolytic process, assumes increased importance.

The effects of temperature and duration of the regime on the rate of formation of diffusion layers are shown in Fig. 95.

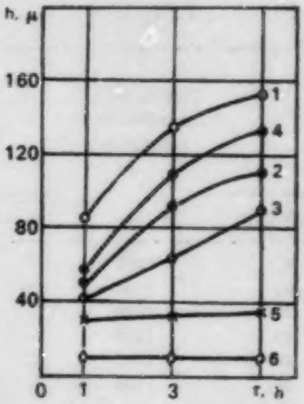

Fig. 95. Effect of temperature and duration of diffusion coating on the thickness of molybdenosiliconized layers on Armco iron:

1—1100°C; 2—1050°C; 3—1000°C; 4—steel 20 (1100°C); 5—steel 45 (1100°C); 6—steel 45 (1050°C).

Melt: 50 mol% $Na_2SiO_3 + 50\%$ Na_2MoO_4.

At all the investigated temperatures the diffusion coating, formed on Armco iron, consisted of α-solid solution of molybdenum and silicon in iron.

Such diffusion layers are fairly thick (under the investigated regime parameters they varied from 40 to 150 μ.

Irrespective of the parameters of the regime (temperature, time, composition of the melt) the quantity of silicon involved in formation of the diffusion layer is small: the silicon concentration at the surface of the diffusion layer does not exceed 1%, whereas the concentration of molybdenum, depending on the parameters of the process, fluctuates between 3.5 to 7.5% (Table 63). A low and constant concentration of silicon in the diffusion layer, according to the authors of [342], is due to the higher chemical affinity of silicon for molybdenum than for iron. Consequently, the quantity of silicon involved in the formation of the diffusion layer is controlled by the process of formation of silicides of molybdenum in the melt.

On low- and medium-carbon steels (steel 20 and steel 45), at 1000 and 1050°C, the diffusion layer consists of a thin crust of molybdenum carbide—Mo_2C. The thickness of the carbide layer does not exceed 10–15 μ. In the case of molybdenosiliconizing of steel 45 at 1100°C, the diffusion layer comprises two zones: external—carbide (Mo_2C), and internal—α-solid solution. The diffusion layer formed on steel 20, at 1100°C, consists of α-phase with inclusions of carbide Mo_2C, and an intermetallic compound, Fe_7Mo_6 [342].

Table 63

Compositions of melt, mol%		Temperature at diffusion saturation	Concentration of elements on surface of molybdenosiliconized coating on Armco iron, %	
Na_2SiO_3	Na_2MoO_4		Mo	Si
20	80	1000	5.2	1.08
20	80	1100	5.7	0.97
50	50	1000	6.1	1.1
50	50	1100	7.2	1.0
80	20	1000	5.0	0.89
80	20	1100	6.2	0.99

In order to identify the role of silicon in the formation of Mo_2C, the authors [342] carried out x-ray diffraction investigations on the lattice parameters of the unit cells of carbides formed during molybdenizing and molybdenosiliconizing (Table 64). Determination of the parameters was conducted on an URS-50IM type diffractometer using the (112) line.

Table 64

Method of obtaining Mo_2C phase	Reference	Lattice parameters, Å		
		a	*c*	*c/a*
Molybdenizing	[342]	3.006	4.723	1.571
Molybdenosiliconizing	[342]	3.006	4.745	1.578
Synthetic	[367]	3.002	4.724	1.574

Increase in parameter 'C' during molybdenosiliconizing is related to the substitution of carbon atoms by silicon atoms.

Carbon sharply reduces the thickness of the α-phase layer. A continuous carbide layer, at 1050°C, is formed on the surface of steels containing 0.18–0.2% or higher concentration of carbon.

An increase in the carbon concentration of steel is accompanied by an increase in thickness of the carbide layer on the surface. Qualitatively, the effect of carbon on the thickness of a diffusion-saturated molybdenosiliconized layer is similar to that observed in molybdenizing (Fig. 96).

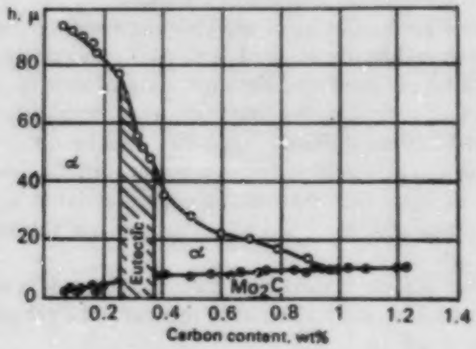

Fig. 96. Effect of carbon concentration in steel on depth and structural constituents of molybdenosiliconized layer.

Molybdenosiliconized coatings on Armco iron reveal a tendency toward dispersion hardening [342]. Specimens subjected to diffusion saturation in a melt containing 50% Na_2SiO_3 + 50% Na_2MoO_4 at 1100°C for 4 h, subsequently water quenched from the treatment temperature and age hardened for 1.5 h at 640°C, had a hardness of 720 kgf/mm², whereas tempered specimens revealed a hardness of only 250 kgf/mm². The parameters of dispersion hardening given here, are those which were found to be optimum (Fig. 97).

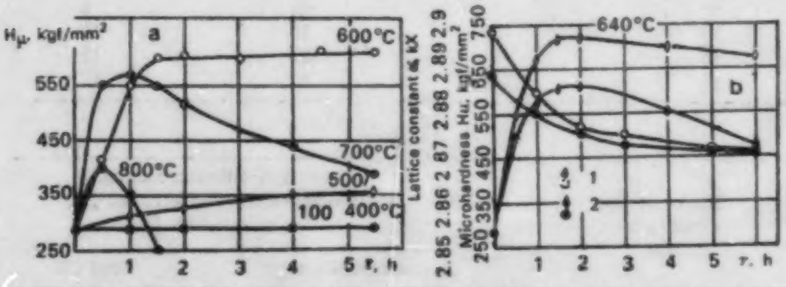

Fig. 97. (a) Effect of temperature and duration of age hardening on microhardness of molybdenosiliconized layers. (b) Effect of duration of age hardening at 640°C on lattice parameters of solid solution and microhardness: 1—molybdenosiliconizing; 2—molybdenizing.

The strengthening phase is, most probably, the intermetallic compound Fe_2Mo. This view is widely supported by investigators who have studied age hardening of molybdenized and molybdenosiliconized iron.

The phenomenon of age-hardening is more pronounced in molybdenosiliconized layers, than in molybdenized layers. On age-hardening of molybdenized layers at optimum temperature (610°C) the resultant hardness of the diffusion layer does not exceed 620–630 kgf/mm^2.

The process of age-hardening of molybdenized and molybdenosiliconized diffusion layers should be investigated in an inert atmosphere.

α-solid solutions obtained by diffusion coating of iron, in melts containing less than 5 mol% of sodium molybdate, were not amenable to age-hardening.

Molybdenosiliconized diffusion layers can also be obtained without the application of an external electric field, i.e. by the introduction of a sufficiently strong reducing agent (for example, calcium silicide) in a melt containing 50% of Na_2SiO_3 and 50% of Na_2MoO_4. The results obtained are similar to those described above.

When calcium silicide is used as a reducing agent, it is not necessary to add Na_2SiO_3 to sodium molybdate, as in this case, the reducing agent itself acts as a source of silicon.

The maximum efficiency of diffusion coating is exhibited by a sodium-molybdate melt containing 15% (by weight) of calcium silicide (Table 65) the size of the granules being between 0.32–0.63 mm (Table 66).

Table 65

Composition of melt, wt. %		Thickness of molybdenosiliconized layer, μ ($t=1050°C$, $\tau=4$ h)	
Na_2MoO_4	calcium silicide—I	commercial iron	steel U8
95	5	40	8
90	10	55	10
85	15	60	12
80	20	60	12

Table 66

Size of calcium silicide grains, mm	Thickness of diffusion coating, μ ($t=1050°C$, $\tau=4$ h) of 15 wt.% calcium silicide I	
	commercial iron	steel U8
>0.2	65	7
0.32–0.63	90	14
1.0–1.4	70	12

The rate of formation of the diffusion layer in this melt is comparable with the rate of formation of the surface layer during electrolytic molybdenosiliconizing (Table 67).

Table 67

Parameters of molybdenosiliconization (15 wt.% of calcium silicide—I)		Thickness of diffusion coating, μ	
t °C	τ, h	Armco iron	steel U8
950	2	25	5
	4	35	7
	6	42	9
1000	2	42	7
	4	58	10
	6	72	12
1050	2	68	14
	4	120	20
	6	154	24

The structure of the diffusion layer formed during molybdenosiliconizing of plain carbon steels in melts containing 85% of sodium molybdate and 15% of calcium silicide—I is typical for molybdenosiliconized coatings and consists of a carbide layer (Mo_2C, possibly Fe_2Mo_2C) and α-solid solution of molybdenum and silicon in iron. The diffusion layer formed on Armco iron consists of only α-solid solution of molybdenum and silicon in iron.

The surface hardness of molybdenosiliconized layers on steel 45 reaches 1250–1300 kgf/mm². According to the data given by Kasachevskii [342], the hardness of the intermetallic phase beneath the carbide layer is found to be 280–300 kgf/mm². As indicated earlier, the hardness of α-phase on Armco iron can be increased by age hardening to 700–720 kgf/mm². Such a high hardness of the molybdenosiliconized layer indicates that it should have a high wear resistance.

It has been shown [342] that molybdenosiliconized coatings on Armco iron and plain carbon steels fail to protect them from corrosion in 10% dilute acids (HNO_3, HCl, H_2SO_4) solutions of salts (NaCl) and dilute alkali (NaOH). The low corrosion resistance of electrolytically molybdenosiliconized steel 45 could, most probably, be due to an inadequate continuity in the carbide layer, as it is well established that molybdenum carbide, Mo_2C, is highly stable against attack by cold and boiling hydrochloric acid (density 1.19 g/cm³), cold sulfuric acid (density 1.84 g/cm³), cold and boiling phosphoric acid (density 1.21 g/cm³) and a 20% solution of sodium hydroxide at room temperature as well as at boiling point [343].

The heat resistance of iron and steels remains practically unchanged after molybdenosiliconizing.

3. TUNGSTENOSILICONIZING

Tungstenosiliconized diffusion coatings can be produced either by electrolysis of melts of the Na_2SiO_3–Na_2WO_4 system or by chemical reduction of these melts using active reducers.

When calcium silicide is used as a reducer, it is not necessary to add sodium monosilicate to the Na_2WO_4 melt as the reducer itself acts as a source of silicon.

Surface alloying is carried out at 1000–1100°C. The duration of the process depends on the thickness of the diffusion coating required. The current density during electrolytic tungstenosiliconizing was maintained at 0.2–0.3 A/cm^2. The tungstenosiliconized diffusion coating formed on Armco iron by electrolyzing a melt containing up to 85% of sodium monosilicate was found to be similar to tungstenized layers as far as age hardening is concerned. The concentration of tungsten reaches 6–8%, whereas it does not exceed 0.5–0.7 wt.% for silicon.

In steel containing 0.2% or more of carbon, a dense continuous layer of carbide, W_2C, is formed on the surface of the diffusion layer. Its thickness increases with increase in the carbon concentration in steel, whereas the thickness of the α-phases is sharply reduced with an increasing carbon content in the steel.

A diffusion layer does not form in the concentration interval of Na_2SiO_3 between 85–95 mol%. At higher concentrations of sodium monosilicate in the melt a siliconized layer consisting of acicular grains of α-phase is formed.

In electroless liquid-phase tungstenosiliconizing, it is necessary to add 10–15% of calcium silicide I (Table 68) to a melt containing Na_2SiO_3–Na_2WO_4 or to a pure sodium molybdate melt.

The optimum size of calcium silicide granules was found to be 0.32–0.63 mm. The diffusion layer formed on the surface of Armco iron by carrying

Table 68

Calcium silicide content of the melt, %	Thickness of the diffusion layer, μ (1050°C, 4 h)	
	Armco iron	steel U8
5	35	4
10	55	6
15	60	8
20	60	8

out surface alloying in a melt of optimum composition (85% Na_2WO_4+15% calcium silicide I) consists of α-solid solution of tungsten and silicon in iron. In plain carbon steels the carbide layer forms at the surface (based on the carbide, W_2C) and beneath it forms the α-solid solution.

The effect of temperature and duration of the process on the thickness of the tungstenosiliconized layer are shown in Table 69.

Table 69

Parameters of tungstenosiliconizing		Thickness of diffusion coating, μ (calcium silicide 15%)		
		Armco iron (α-solid solution)	steel U8	
t, °C	τ, h		carbide	α-solid solution
950	2	21	2.5	—
	4	28	4.5	—
	6	35	6	3
1000	2	26	4	—
	4	42	6	7
	6	55	8	14
1100	2	80	9	14
	4	120	14	21
	6	140	17	21

The rate of formation of the diffusion layer, on simultaneous surface impregnation of iron (steel) with tungsten and silicon, was found to be significantly higher than that observed on pure tungstenizing (Table 70).

Hardly any investigations have been carried out on the properties of a tungstenosiliconized coating. Only a high hardness and wear resistance of carbide layers formed on medium and high-carbon steels by simultaneous diffusion saturation of tungsten and silicon have been reported.

Surface alloying of iron and steel with tungsten and silicon does not improve their heat resistance.

4. TITANOSILICONIZING

Titanosiliconizing leads to an improvement in surface hardness and heat and corrosion resistance of metals and alloys in different corrosive mediums.

Simultaneous diffusion saturation of surface layers of steels is carried out in powder mixtures of titanium and silicon (or their ferroalloys) as well as in powders of specially prepared alloys of titanium and silicon [1, 20, 24, 302, 304, 313, 344, 346–353]. Halides are used as activators (NH_4Cl, AlF_3, NaF

Table 70

Parameters of electrolytic tungstenizing		Thickness of diffusion layer, μ		
		Armco iron (α-solid solution)	steel U8	
t, °C	time, h		carbide	α-solid solution
1000	2	10	4	—
	4	16	7	—
	6	20	8	—
1050	2	12	5	—
	4	18	8	—
	6	22	9	4
1100	2	28	7	—
	4	40	10	5
	6	46	12	7

and others) and refractory oxides (Al_2O_3, ZrO_2, MgO) are employed as inert additives to prevent sintering of the active mixture.

The diffusion coating >0.8 mm thick obtained by surface alloying in a powder mixture containing 40% of Ti, 14% Si, and 46% Fe followed by annealing it four times for five hours each at 1150°C, was found to contain a large number of pores mainly concentrated near the surface. Finer pores were observed in a zone of the layer in immediate contact with the interface between the alloyed ferrite formed during diffusion saturation and the austenite which, on cooling, transforms to ferrite. An impervious coating on iron is formed in powder mixtures of titanium and silicon with minor additions such as chromium, molybdenum, tungsten or tantalum.

Zemskov et al. [1, 20, 24, 313] have investigated titanosiliconizing of ZhS6K alloy in powder mixtures of silicon and titanium contained in vessels with fusible seals, in the temperature interval of 850 to 1200°C and a duration of impregnation ranging between 10–15 h. Ammonium chloride was used as an activator. It was observed that the increase in silicon content in the active mixture is accompanied by an increase in the thickness of the diffusion layer. Simultaneous surface alloying of ZhS6K alloy with titanium and silicon was carried out in mixtures containing 35–90% of titanium. A siliconized coating was formed on the surface in cases where the concentration of titanium in the mixture was less than 35% whereas pure titanizing of the surface took place when the titanium concentration in the mixture exceeded 90%.

The microhardness of the surface zone of the titanosiliconized layer decreases with an increasing concentration of titanium in the active mixture.

The concentration of silicon and titanium in the surface zone of diffusion-saturated coatings were found to be 12.6 and 7%, respectively [1].

The authors of [1, 20, 24, 313] have recommended that titanosiliconizing should be conducted in powder mixtures containing 60 to 80% of Ti and 20–40% of Si, at 900°C.

For titanosiliconizing an aluminothermic method can also be employed. From thermodynamic considerations it has been shown that the concentration of aluminum in aluminothermic mixtures should be 25%. On increasing the ratio of $SiO_2 : TiO_2$ in the mixture from 1 : 9 to 1 : 4 the thicknesses of titanosiliconized coatings on Armco iron and plain carbon steels are found to improve.

From the point of view of heat resistance, the following composition of the mixture for titanosiliconizing has been found to be most suitable:

$$100\% \{40\%\ Al_2O_3 + 60\%\ [25\%\ Al + 75\%\ (85\%\ TiO_2 + 15\%\ SiO_2)]\} + 2\%\ NH_4Cl.$$

The effect of the duration of treatment on the thickness of titanosiliconized layers (produced by using a mixture of optimum composition) is shown in Fig. 98. After simultaneous diffusion saturation of Armco iron with titanium and silicon for 8 h at 1100°C, it was observed that the silicide zone of Ti_5Si_3 and Fe_5Si_3 which is in contact with the zone of acicular crystals of the solid solution of titanium and silicon in α-iron with fine-disperse precipitates of the excess phase (which, probably, is made up of silicides of iron and titanium).

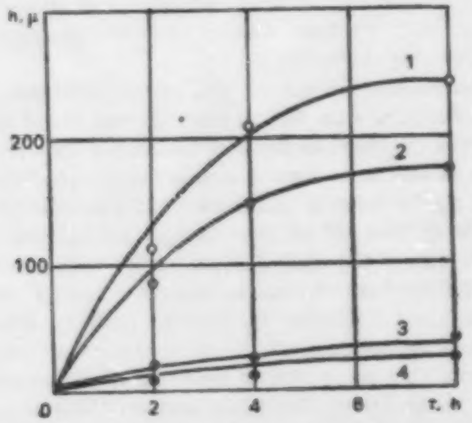

Fig. 98. Effect of duration of diffusion saturation on thickness of titanosiliconized layers:

Mixture composition: 98% $\{40\%\ Al_2O_3 + 60\%\ [25\%\ Al + 75\%\ (85\%\ TiO_2 + 15\%\ SiO_2)]\} + 2\%\ NH_4Cl$. 1—Armco iron; 2—steel 20; 3—steel 45; 4—steel U8.

A diffusion coating on steel 45 or steel U8 consists of three zones: a carbide zone (Ti, Fe)C; a silicide zone Fe_5–Si_3 and Ti_5–Si_3, isomorphous with Ti_5Si_3 and a zone of solid solution of titanium and silicon in α-iron.

The concentration of titanium and silicon on the surface of titanosiliconized steel 45, after surface impregnation in mixtures of optimum composition for 8 h at 1100°C, was found to be 52 and 10.0%, respectively.

On analysis of the charge after diffusion saturation, small quantities of Ti_5Si_3 were traced in it.

The structure of titanosiliconized layers changes with a variation in the SiO_2 content of the charge. When silica and titanium are in the ratio of 1 : 4, an α′-phase layer consisting of Fe_3Si is formed on the surface of iron and plain carbon steels. The formation of Fe_3Si sharply increases the brittleness of the diffusion layer.

In the literature very little data is available in regard to the effect of simultaneous surface impregnation with titanium and silicon on the mechanical properties of metals and alloys. According to Pentecost [351], the microhardness of a titanosiliconized coating on iron gradually decreases from 300 kgf/mm² (at ~0.1 mm below the surface) to 170 kgf/mm² at the interface between the ferrite alloyed with silicon and titanium and the core metal. The microhardness of the surface zone with a thickness of 0.1 mm could not be measured due to its very high porosity.

Diffusion coatings produced by aluminothermic reduction of TiO_2 and SiO_2, consisting of solid solution of titanium and silicon in α-iorn (coating on Armco iron) have a microhardness of the order of 285–260 kgf/mm² in the zone adjoining the silicide zone and 200–180 kgf/mm² in the vicinity of the interface with the core metal. The microhardness of the silicide $(Ti, Fe)_5Si_3$ is 950–1000 kgf/mm².

The microhardness of the thin layer of carbide (TiC and FeC) on the surface of titanosiliconized steel 45 and steel U8 was found to be 1950–2130 kgf/mm², whereas the microhardness of the silicide zone (Fe_5Si_3 and Ti_5Si_3) on these steels as well as on Armco iron is found to be 945–1000 kgf/mm². In the zone of α-solid solution of titanium and silicon in iron the hardness decreases gradually from 350 kgf/mm² to $H_{50} = 210$ kgf/mm².

Diffusion layers of titanium disilicide $TiSi_2$ with a microhardness of $H_{50} = 800$–850 kgf/mm² are obtained by successive surface alloying of ZhS6K alloy with silicon and (followed by) titanium [1, 313]. When ZhS6K alloy was subjected to simultaneous surface impregnation with titanium and silicon in a charge containing up to 30% of titanium, it was observed that silicon diffusion was predominant. The microhardness (H_{50}) of the surface layer was found to be 1100 kgf/mm². Increasing the titanium content in the active mixture beyond 30% led to a reduction in microhardness at the surface [313].

A titanosiliconized diffusion coating on iron slightly improves its heat resistance [351]. According to our data, the improvement in heat resistance of Armco iron and plain carbon steels is less in the case of titanosiliconizing as compared to siliconizing alone.

The results of investigations on heat resistance (over 26 h at 1000°C) of siliconized and titanosiliconized (by an aluminothermic process—8 h at 1100°C) Armco iron and plain carbon steel are reproduced in Table 71.

Table 71

Coating	Weight gain, g/m^2			
	Armco iron	steel 20	steel 45	steel U8
Si	10.8	4.5	20.5	14.7
Ti–Si	296	329	306	283

Diffusion saturation of ZhS6K alloy with silicon and titanium (simultaneous as well as successive), quite dependably, protects it from gas corrosion in an atmosphere of combustion products of sulfurous fuels containing vapors of sea water at 900°C [24, 304, 313].

In untreated specimens a catastrophic failure takes place under these conditions. Thickness of the damaged layer is found to be as much as 1000–1200 μ. The results of comparative testing of one-component (Si, Al, Cr) and two-component titanosiliconized diffusion coatings for their resistance to gas corrosion are shown in Fig. 99. The hatched portion in the diagram corresponds to the damaged part of the layer. The maximum resistance to corrosion is that of titanosiliconized diffusion coatings, obtained by successive surface alloying. Coatings obtained by simultaneous impregnation with silicon and titanium are somewhat inferior to these. One-component coatings (Si, Al, Cr) have a significantly lower corrosion resistance.

Attempts to use titanosiliconizing for protection of steel 45 and steel 3Kh2B8 against attack by liquid aluminum and brass were not successful [348]. Titanosiliconized layers on steel are also wetted and interact with mloten aluminum and brass in the same way as untreated steels.

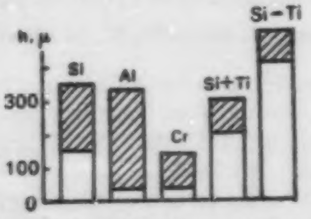

Fig. 99. Results of testing of diffusion coatings on ZhS6K alloy for resistance to gas corrosion in the flow of products of combustion for 15 h at 900°C.

5. ZIRCOSILICONIZING

The process of zircosiliconizing has been studied to a lesser extent as compared to titanosiliconizing. Simultaneous surface alloying of steels with zirconium and silicon improves their resistance to high temperature oxidation and corrosion in different corrosive mediums.

Zircosiliconizing was carried out by E. Fittser by adding zirconium in a charge for siliconizing, in order to reduce the porosity of siliconized diffusion coatings on steel and to produce heat-resistant coatings [351]. However, simultaneous diffusion of silicon and zirconium led to an enhancement in the diffusion porosity in a siliconized diffusion coating.

It is possible to obtain zircosiliconized layers on Armco iron and plain carbon steels by aluminothermic reduction of ZrO_2 and SiO_2 in the active mixture. The effect of the ratio of ZrO_2 and SiO_2 in the charge on the thickness of a zircosiliconized layer is shown in Fig. 100. Increasing the SiO_2 content of the mixture beyond 15% (of the total content of ZrO_2+SiO_2) resulted in a sharp increase in thickness of the diffusion layer owing to the formation of α'-phase, consisting of Fe_3Si, on the surface of iron and steels. The formation of a 'superlattice' took place, probably due to the better reducibility of marshalite silica flour as compared to zirconium oxide.

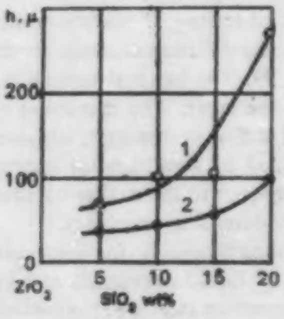

Fig. 100. Effect of concentrations of ZrO_2 and SiO_2 in aluminothermic mixtures on thickness of a zircosiliconized layer on (1) Armco iron and (2) steel U8:

Composition of charge: 40% Al_2O_3, 25% Al, 2% NH_4Cl ($t=1100$°C, $\tau=4$ h).

The variation in the thickness of zircosiliconized layers on iron and plain carbon steels with the duration of treatment in a mixture of optimum composition: 98% {40% Al_2O_3 + 60% [25% Al + 75% (85% ZrO_2 + 15% SiO_2)]} + 2% NH_4Cl at 1100°C is shown in Fig. 101.

The coating formed on the surface of Armco iron consists of a silicide (Zr_5Si_3 and Fe_5Si_3) (isomorphous with the silicide, Fe_5Si_3) with a microhardness of 1000 kgf/mm^2 and solid solution of zirconium and silicon in α-iron with

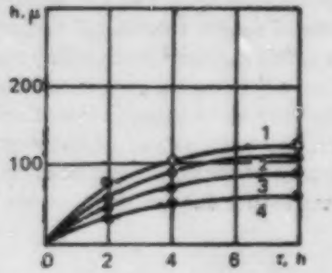

Fig. 101. Effect of duration of treatment on thickness of zircosiliconized layers on (1) Armco iron, (2) steel 20, (3) steel 45 and (4) steel U8:

Composition of charge: 98% {40% Al_2O_3 + 60% [25% Al + 75% (85% ZrO_2 + 15% SiO_2)]} + 2% NH_4Cl, ($t = 1100$°C, $\tau = 4$ h).

an acicular structure (Fig. 102, a). Finely-dispersed inclusions of a precipitated phase, most probably, the silicide, (Fe, Zr)$_5$Si$_3$, are observed in the zone of α-solid solution adjoining the silicide (Zr, Fe)$_5$Si$_3$. The microhardness of solid solution gradually decreases from the surface toward the core of the specimen, varying from 285 to 180 kgf/mm^2.

The surface layer of a zircosiliconized coating on steel 45 and steel U8 is found to consist of: i) a carbide zone of composition (Zr, Fe)C with a microhardness of 1415 to 1650 kgf/mm^2; ii) a silicide zone of composition Fe$_5$Si$_3$

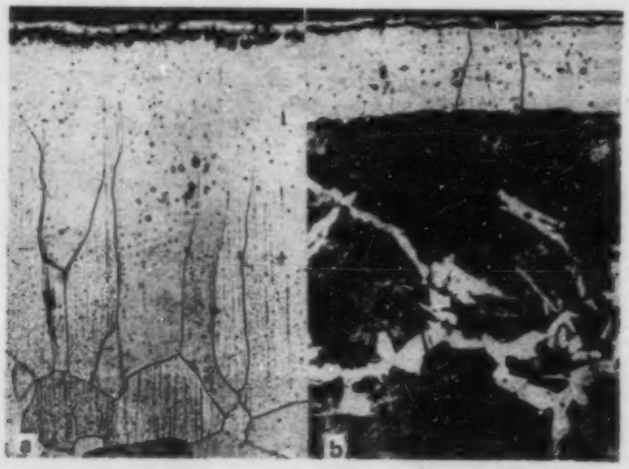

Fig. 102. Microstructure of zircosiliconized coatings:
a—Armco iron; b—steel 45. ($t = 1100$°C, $\tau = 8$ h), ×200.

and Zr_5Si_3 (isomorphous with Zr_3Si_3) with a microhardness of about 1000 kgf/mm^2 and iii) a zone of α-solid solution of zirconium and silicon in iron with a microhardness of 350 kgf/mm^2 in the vicinity of the silicided zone and 210 kgf/mm^2 in the zone adjoining the core metal (Fig. 102, b). The concentration of silicon at the surface of a zircosiliconized layer on steel 45 and found to be 16% (data of spectroscopic analysis). Qualitatively, the presence of zirconium in the surface zone of specimens has been established. (Quantitative analysis could not be carried out due to nonavailability of standard specimens.)

CHAPTER IV

Two-component Coatings Containing Chromium

1. CHROM-MANGANIZING

Simultaneous surface alloying of iron–carbon alloys with chromium and manganese results in improvement of their surface hardness, wear resistance, resistance to pitting and possibly an increase in their corrosion resistance in some corrosive mediums (no data is, however, available on this aspect).

Simultaneous surface impregnation with chromium and manganese can be carried out in powder mixtures mainly consisting of manganese (grade MrO) and ferrochromium (grade Kh75) with small additions of Al_2O_3 and NH_4Cl, contained in metal vessels provided with fusible seals. The compositions of the mixtures investigated are given in Table 72.

Table 72

Number of mixture	Composition of mixture for chrom-manganizing, wt.%			
	Cr	Mn	Al_2O_3	NH_4Cl
1	50	0	50	0
2	40	10	50	0
3	30	20	50	0
4	20	30	50	0
5	10	40	50	0
6	0	50	50	0
7	50	0	50	2
8	40	10	50	2
9	30	20	50	2
10	20	30	50	2
11	10	40	50	2
12	0	50	50	2

Note: NH_4Cl was introduced in addition to 100% of principal charge.

The effect of composition of the charge on the thickness of the surface-alloyed layer was investigated under the following conditions: temperature 1000°C, duration of treatment 6 h. The results obtained are given in Table 73.

Table 73

Number of mixture for chrom-manganizing	Thickness of diffusion coating, μ	
	Armco iron	steel 45
1	41	10
2	19	10
3	29	20
4	29	17
5	35	35
6	—	22
7	20	12
8	20	13
9	35	30
10	35	35
11	38	23
12	45	40

The surface of specimens alloyed with chromium and manganese had a silvery white color.

Typical microstructures of diffusion coatings on Armco iron and steel 45 are shown in Fig. 103.

The coating has a two-phase structure for the ratio of FeCr : Mn varying between 60 : 40 to 0 : 100. From x-ray structural analysis conducted on a DRON-1 unit with an iron target ($V_{scan} = 1°/min$, $V_{chart} = 600$ mm/h), it was found that the diffusion layer on Armco iron obtained by simultaneous surface alloying with chromium and manganese consists of α- and γ-phases (the latter is located in the vicinity of the metal core and is enriched with manganese). Solid solutions with an α- and γ-iron matrix are alloyed with manganese as well as chromium. An increase in the manganese content of α-phase shifts the Bragg diffraction angle of this phase to higher values.

The diffusion coating on steel 45 comprises of a carbide zone and zones of α- and γ-solid solutions. The carbide zone of the layer obtained in active mixtures rich in chromium consists of carbides of chromium, alloyed with manganese and iron and that obtained in mixtures rich in manganese consists of cementite-type carbide $(Mn, Fe)_3C$ alloyed with chromium up to a definite extent.

Unidentified lines in the x-ray diffraction photograph could correspond to the following three phases: $FeMn_3$, $CrMn_3$ and α-manganese. In our opinion, it is preferably the last phase mentioned, namely that of α–Mn.

X-ray structural analysis of the charge, after it has been used for diffusion saturation, indicates the possibility of formation of $CrMn_3$ in it. Investigations on the effect of important factors, such as the temperature and duration

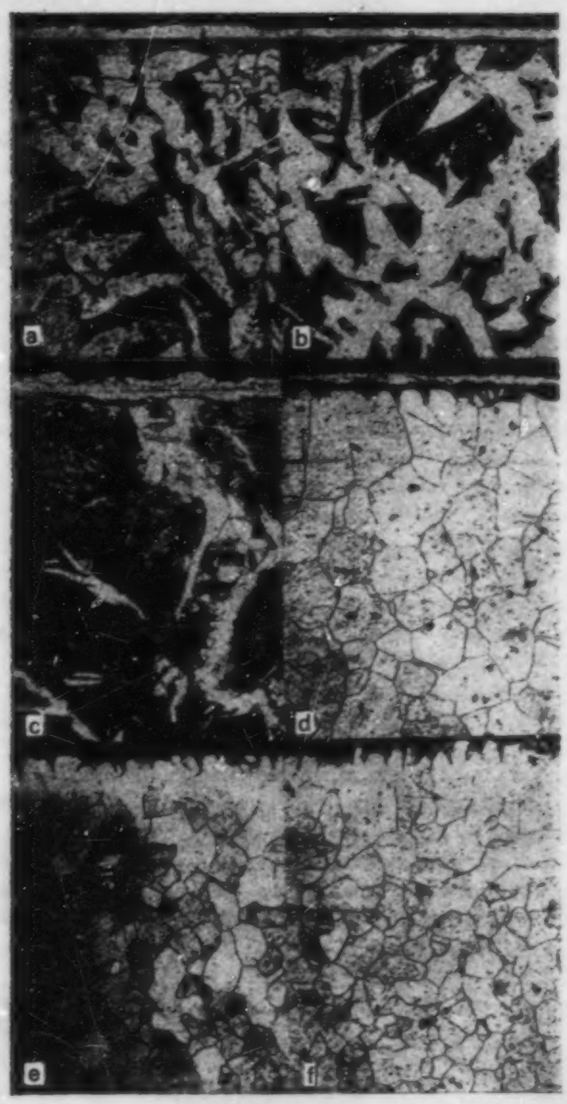

Fig. 103. Microstructure of steel 45 (a, b, c) and Armco iron (d, e, f) (both surface treated with chromium and manganese). Composition of the active mixture (only main constituents are given): a—100% Cr; b—80% Cr+20% Mn; c—60% Cr+40% Mn; d—40% Cr+60% Mn; e—20% Cr+80% Mn; f—100% Mn.

of surface alloying and composition of the mixture (to a limited extent), on the kinetics of formation of the constituent phases and the wear resistance of the coatings produced by simultaneous diffusion of chromium and manganese have been carried out by mathematical modeling of experiments.

An increase in the treatment temperature increases the total depth of surface impregnation as well as the thickness of the carbide zone on steel 45. Though the thickness of the carbide zone on steel U8 appears to be independent of temperature variations, it increases with a prolonged duration of the treatment. A variation in composition of the active mixtures quite significantly influences the kinetics of formation of the diffusion layer on steel U8. An increase in the ferromanganese content of the mixture increases the depth of the diffusion layer in general and the thickness of the carbide zones in particular, whereas an increase in Al_2O_3 has a negative effect. In the case of steel 45, any increase in the ferromanganese content of the mixture increases the total thickness of the coating, but the thickness of the carbide zone remains unchanged. A variation in the quantity of inert material does not reveal any significant effect on the thickness and structural composition of the diffusion coating on steel 45. On increasing the duration of treatment the thickness of the diffusion coating on steel 45 increases mainly due to the increase in the zone of solid solution whereas on steel U8 improvements in the thickness of the carbide zone and increase in the thickness of the zone of solid solution are both equally responsible for the increase in aggregate thickness.

The wear resistance of plain carbon steels, simultaneously surface impregnated with chromium and silicon, are most strongly influenced by the treatment temperature and the quantity of inert material in the charge. The effect of variations in the concentrations of ferromanganese and activators in the mixture are somewhat moderate.

Investigations on wear resistance were carried out on a Skoda-Savin type unit. The specimens, simultaneously surface impregnated with chromium and silicon, were air cooled from the temperature of impregnation in the containers themselves, and were not subjected to any further heat treatment.

Best results were obtained under the following conditions: steel 45—$t=1050°C$, $\tau=6.5$ h, composition of the mixture—97% (34% Mn_5 + 17% Al_2O_3 + 49% Kh75) + 3% NH_4Cl; steel U8—$t=1030°C$, $\tau=6.5$ h, composition of the mixture (40% Mn5, 18% Al_2O_3 + 42% Kh75) + 3.5% NH_4Cl.

The wear rate of coatings produced under optimum conditions (as mentioned above) was found to be 0.71 and 0.67 mm^3 for steel 45 and steel U8, respectively. For comparison, data on wear resistance of a few tool steels and structural steels are given in Table 74. Thus, it can be seen that even without subsequent heat treatment, diffusion saturation with chromium and silicon can improve the wear-resistance of plain carbon steels (steel 45 and steel U8) by approximately 2.5 times as compared to that observed when they are hardened tempered at a low temperature.

Table 74

Grade of steel	Wear, mm³ after hardening and low-temperature tempering
Steel 45	1.90
Steel U8	1.6
Steel khVG	1.8
7Kh3	1.84
Kh12F1	2.0
25Kh5MA	1.12

The wear resistance of coatings produced by surface impregnation of chromium and manganese is determined mainly by the thickness of the carbide zone and should improve with an increase in the carbon concentration of the steel (this has also been experimentally confirmed).

Simultaneous surface alloying of plain carbon steels with chromium and manganese protects them from high-temperature oxidation. There is a gradual improvement in the characteristics of heat resistance while proceeding from a chrom-manganese coating to pure chromizing.

2. CHROMTITANIZING

Simultaneous surface alloying with chromium and titanium ensures heat-resistant coatings on steels and alloys and improves the durability of the stamping components used for hot upsetting and pressure forming of aluminum castings and aluminum alloys in a press.

Surface impregnation with chromium and titanium is carried out either in powder mixtures of pure metals [1, 20, 24, 344, 345, 347] or oxides of metals which are reduced with aluminum [102]. Aluminum oxide and some halides are also added in the active mixture.

Simultaneous surface impregnation with chromium and titanium takes place in powder mixtures of elements containing 10 to 30% of chromium. At lower concentrations of chromium, a preferred diffusion impregnation with titanium takes place and, at higher concentrations, chromium is predominant. On varying the chromium concentration in the active mixture from 10 to 30%, a gradual increase in the thickness of the diffusion coating is observed (Fig. 104) [20].

The thickness of chromtitanized coatings on steel is found to be considerably lower than those in iron. In the surface layers of steels, a carbide diffusion layer is formed [1].

For surface alloying of iron and steel with chromium and titanium,

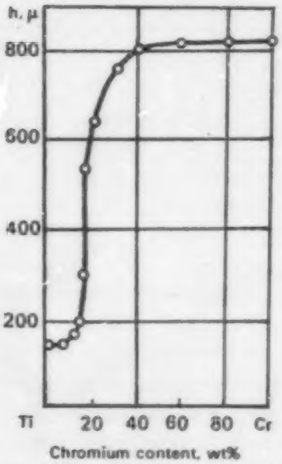

Fig. 104. Dependence of thickness of diffusion layer on ratio of titanium and chromium in a powder mixture: $t=1000$°C.

aluminothermic mixtures containing Cr_2O_3, TiO_2, Al_2O_3, aluminum powder and ammonium fluoride have also been used.

The effect of the concentration of aluminum on the thickness of the diffusion layer in the proportion $Cr_2O_3 : TiO_2 = 70 : 30$ is shown in Fig. 105. Simultaneous surface impregnation with chromium and titanium takes place in

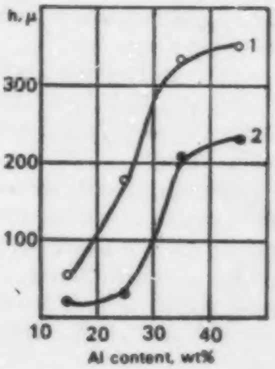

Fig. 105. Effect of aluminum concentration in an active mixture on thickness of Cr–Ti coatings:

$Cr_2O_3 : TiO_2 = 70 : 30$, $Al_2O_3 = 40\%$, $AlF_3 = 5\%$ $\tau = 4$ h, $t = 1100$°C. (1—Armco iron; 2—steel 45).

mixtures containing up to 25% of Al. Under these conditions, a carbide diffusion layer is formed on steel U8, whereas on Armco iron it consists of a solid solution of titanium and chromium in α-iron. In active mixtures, with aluminum concentrations exceeding 25%, the layer formed on iron as well as on plain carbon steel consists of solid solution of aluminum, chromium and titanium in α-iron which is accompanied by a sharp increase in the thickness of the diffusion layer.

Figure 106 indicates the variation in the thickness of Cr–Ti coatings with the duration of treatment in mixtures with $Cr_2O_3 : TiO_2 = 70 : 30$ and containing 15% and 25% of aluminum. It can be seen that the activity of the mixture significantly improves with an increase in its aluminum content.

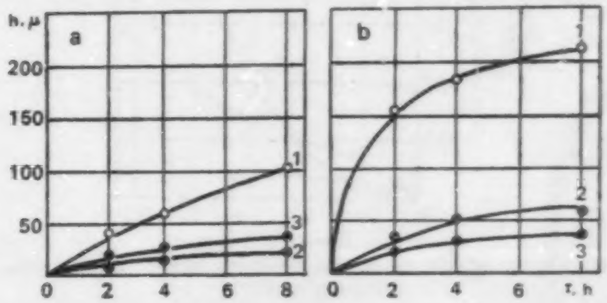

Fig. 106. Effect of duration of treatment on thickness of surface-alloyed layers: $t = 1100$°C, $Cr_2O_3 : TiO_2 = 70 : 30$, Al_2O_3—40%, $AlF_3 = 5\%$ (1—Armco iron; 2—steel 45; 3—steel U8; a—15% Al; b—25% Al).

Surface alloying of steel 45 with chromium and titanium in active mixtures of 95% {40% Al_2O_3 + 60% [15% Al + 85% (70% Cr_2O_3 + 30% TiO_2]} + 5% AlF_3, results in a carbide layer with concentrations of titanium and chromium in it of 0.55 and 60.9%, respectively. Beneath the zone of carbides $(Cr, Fe)_{23}C_6$ and $(Cr, Fe)_7C_3$, alloyed with titanium, lies the α-solid solution, eutectoid and decarburized zones. Consequently, structurewise, there is little difference between chromized and chromtitanized layer.

On the surface of iron, there exists a thin (2–3 μ) brittle layer of σ-phase along with α-solid solution of chromium and titanium in iron.

The thickness of a coating on ZhS6K alloy produced by surface alloying with chromium and titanium in powder mixtures of pure elements with additions of Al_2O_3 and halides, in containers provided with fusible seals, gradually increases with a rise in the titanium content of the active mixture [20]. Simultaneous diffusion saturation with chromium and titanium took place in mixtures containing 15–50% of Ti. The concentration of chromium and titanium in the surface layer was found to be 59 and 10%, respectively. In the structure of the diffusion layer, an intermetallic compound, Cr_2Ti, (68.47% Cr) was observed in the chromium-base solid solution.

Results of investigations on the kinetics of oxidation of Cr–Ti coated iron (coating produced by diffusion saturation by an aluminothermic method) are given in Fig. 107. The maximum resistance to oxidation is that of coatings produced in mixtures in the ratio of $Cr_2O_3 : TiO_2 = 70 : 30$ containing 15% of Al.

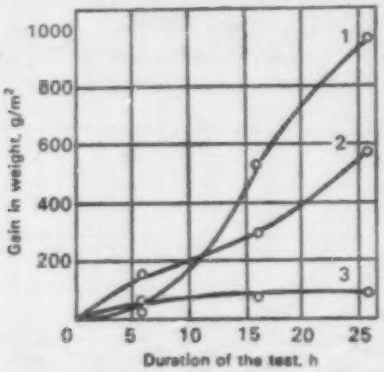

Fig. 107. Kinetics of oxidation of iron surface impregnated with chromium and titanium at 1000°C:

1—Al=25%, $Cr_2O_3 : TiO_2 = 50 : 50$; 2—Al=25%, $Cr_2O_3 : TiO_2 = 70 : 30$; 3—Al=15%, $Cr_2O_3 : TiO_2 = 70 : 30$. Other parameters of impregnation regime: $t = 1000$°C, $\tau = 8$ h, $Al_2O_3 = 40$%, $AlF_3 = 5$%.

Short-duration (26 h) tests at 1000°C have shown that coatings on iron and plain carbon steels obtained by surface impregnation with chromium and titanium in aluminothermic mixtures, oxidize at a faster rate than chromized layers (Table 75).

The results of investigations on chromized and Cr–Ti coatings on alloy steels for 150 h at 1000°C are given in Table 76. Simultaneous surface

Table 75

Coating	Principal constituents of active mixture	Weight gain, g/m² on steel tested for 26 h, at 1000°C			
		Armco iron	steel 20	steel 45	steel U8
Cr	FeCr	6.5	9.4	5.8	17.4
Cr	Cr_2O_3	37.2	98.7	28.4	26.7
Cr–Ti	$Cr_2O_3 + TiO_2$	87.5	160.0	81.0	100.0

Table 76

Substrate metal	Coating	Weight gain, g/m^2 for duration of testing, h							
		6	26	46	66	86	100	120	150
20Kh3MVF	Cr	6.2	12.0	16.8	31.1	80.6	155.9	layer ineffective	
	Cr–Ti	7.8	71.1	296	754	1422	1975	"	
2Kh13	Cr	6.9	10.9	22.1	25.4	32.3	35.2	38.3	44.9
	Cr–Ti	6.3	9.1	11.9	13.2	16.0	16.4	19.2	24.2
Kh25T	Cr	4.7	11.9	14.4	17.4	19.3	20.7	29.2	38.0
	Cr–Ti	4.0	11.2	16.8	20.6	23.4	26.4	29.1	32.4
Kh18N9T	Cr	12.7	16.8	28.4	34.9	40.3	43.9	47.7	54.1
	Cr–Ti	3.8	7.8	9.9	12.7	15.5	16.4	18.9	25.8
3Kh19N9MVBT	Cr	7.1	29.3	44.0	63.8	82.1	97.3	106.1	114.4
	Cr–Ti	3.7	18.6	35.8	60.3	82.9	100.6	109.9	120.0
EI-867	Cr	15.5	25.7	28.7	36.0	46.3	49.5	49.6	50.9
	Cr–Ti	7.5	15.6	18.3	24.5	29.3	34.1	34.4	36.5

impregnation of steels of grades 2Kh13, Kh25T and Kh18N9T, with chromium and titanium improves their heat resistance to a much greater extent than that obtained by chromizing. The rate of oxidation of chromized and Cr–Ti coatings on 3Kh19N9MVBT alloy was practically identical.

Chromtitanized layers (produced by an aluminothermic process) on ZhS6K alloy had a higher heat resistance than that of chromized coatings (Table 76).

According to the data provided by Samsonov and Glukhov [24] coatings produced by surface impregnation of ZhS6K alloy with chromium and aluminum were of a greater thickness than those produced by chromizing under identical conditions and oxidized at a faster rate. It can be assumed that the higher heat resistance of Cr–Ti coatings on ZhS6K alloy is connected with its surface alloying, not only with chromium and titanium but also with aluminum (as the diffusion coating is produced by an aluminothermic process).

Investigations have revealed that coatings formed on ZhS6K alloy by surface alloying with chromium and titanium are in no way inferior to aluminized and aluminosiliconized coatings, as far as the following properties are concerned: heat resistance, thermal shock resistance, erosion resistance, as well as the influence of the coating on the creep resistance of the substrate metal.

Chromtitanized matrix for hot upsetting, made out of 3Kh2V8 steel and tested at the Minsk Tractor Plant were found to be 2.7 to 4.1 times more durable.

Diffusion impregnation of inserts and nozzles made of 3Kh2B8 and 40Kh5MFC steels for casting aluminum alloys under pressure increased their service life by 2–3 times.

3. CARBOCHROMIZING

In spite of the wide application of the carburizing and chromizing process in industry, simultaneous diffusion saturation of steels and alloys with carbon and chromium has been attempted only under laboratory conditions.

Simultaneous surface impregnation of steels and alloys with carbon and chromium improves their hardness, wear resistance and corrosion resistance in different corrosive mediums.

Successive diffusion saturation of steel with carbon and chromium is practiced in industry. Good results were obtained in cases where the steel was first carburized and then subjected to chromizing [101, 276, 284, 355, 359, 360]. Such a technique prevents the formation of a softened decarburized zone beneath the carbide layer and promotes the formation of a carbide layer thicker than that obtained during chromizing. During this, there is a substantial increase in the thickness of the carbide layer consisting of ($Fe_{23}C_6$ and $Cr_{23}C_6$) with a much higher microhardness.

Application of the successive carburizing-chromizing process is recommended for increasing the abrasion and wear resistance of components [101, 284, 359] such as forged steel molds used for casting aluminum under pressure (such molds are exposed to increased wear in the absence of impact loads [355]), for improving their corrosion and fatigue resistance (strength) in a 3% aqueous solution of sodium chloride [276, 360].

Attempts to carburize steel after chromizing were unsuccessful as the formed diffusion layer was found to be brittle as well as porous [101]. In our opinion, even by successive diffusion saturation of steels with chromium and carbon it should be possible to produce coatings which would have practical applications. It is known that carburizing of high-chromium steel provides a diffusion layer on its surface. This surface-impregnated coating is characterized by a large thickness with a high concentration of fine carbide inclusions ensuring a very good bonding with the substrate metal and a high hardness (63–67 HRC). Such coatings are already in use in industry. The use of punches for stamping made of carburized chromium (stainless) steel (grade Kh13) used for the manufacture of various components improves their durability by 2–3 times. A similar diffusion layer can probably be obtained during carburizing of prechromized low-carbon steels with a structure of solid solution of chromium in ferrite and a low (10–20%) concentration of chromium on the surface.

Results of simultaneous diffusion saturation of steels with carbon and chromium, using active powder mixtures containing ferrochromium or chromic oxide as chromium-bearing material and carbon in the form of graphite or barium carbonate, have been described by Dubinin [101].

Introduction of 3.5 and 8% of carbon in mixtures for chromizing (50% FeCr, 45% Al_2O_3 and 5% NH_4Cl) resulted in some improvement in the thickness of carbide layers produced by treatment for 8 h at 1100°C. The use of chromium-oxide base mixtures containing 5 to 6% of carbon added in the form of graphite or pieces of coke, at 1100°C, ensured a carburized coating on the surface of iron and plain carbon steel. Further, additions of barium carbonate in such mixtures led to the formation of a carbide diffusion layer [101].

At the same time, many investigators [284 and others] are of the view that, for diffusion chromizing of steel, it is necessary to use ferrochromium containing not more than 1–1.5% of carbon, as higher concentrations of carbon in ferrochromium lead to a considerable reduction in the thickness of the chromized leyer.

A study of the process of carbochromizing in powder mixtures with the composition of the active mixtures varying from 'pure' chromizing to 'pure' carburizing will be of considerable interest.

If the interaction between chromium and carbon in the mixture and the difference in the characteristics of carbon and chromium, as far as their adsorption on the surface of the metal is concerned, are neglected, then it can be assumed that the ratio of chromium and carbon being deposited on the surface of the substrate during carbochromizing is determined by their concentrations in the powder mixture.

From the Fe–C–Cr phase diagram [365], it follows that the variation in the ratio of chromium and carbon in the surface layer of steel specimens at the treatment temperatures can lead to the formation of two-phase layers (carbide + austenite alloyed with chromium). In these coatings, the following carbide phases may be present: $(Fe, Cr)_3C$ (at $Cr : C \leqslant 4 : 1$); $(Fe, Cr)_7C_3$ (at $4 : 1 \leqslant Cr : C \leqslant 46 : 6$) and $(Fe, Cr)_{23}C_6$ (at $46 : 1 \leqslant Cr : C \leqslant 72 : 1$). At 1000°C the equilibrium composition of the austenite in contact with different carbides is found to be as follows: with carbide $(Fe, Cr)_3C$—$\leqslant 3\%$ Cr, 0.8–1.3% C; with carbide $(Fe, Cr)_7C_3$—3–11.5% Cr, 0.25–0.8% C and with carbide $(Fe, Cr)_{23}C_6$—11.5–14.5% Cr, 0.2–0.25% C.

These austenite-carbide diffusion coatings on medium carbon and low-carbon steels (this type of layer forms on carburizing chromium steels and has a high hardness and wear resistance after heat treatments) are of great practical importance. However, it should be noted that the probability of formation of two-phase austenite-carbide layers of large thickness during carbochromizing is quite low owing to the lower diffusional mobility of chromium as compared to carbon. The maximum hardness and wear resistance of tempered layers can be expected, in such a case during diffusion saturation in addition to carbon austenite dispersible carbides $(Fe, Cr)_3C$ and $(Fe, Cr)_7C_3$ are also formed in the two-phase diffusion layer.

Results of metallographic investigations on the structure of carbochromized layers produced by simultaneous surface alloying of steel 15, steel 40Kh, steel ShKh15 and steel 5KhNV, with carbon and chromium in powder mixture the composition of which was varied from that of a pure chromizing mixture to a pure carburizing mixture, have been shown by us in the form of phase diagrams representing the effect of the composition of the active mixture and the duration of treatment on the thickness of different zones of the layers [363, 364]. As an example, two such phase diagrams for carbochromized coatings on steel 15 and steel ShKh15 (temperature of impregnation 1100°C) are shown in Figs. 108 and 109.

A powder mixture consisting of 60% of ferrochromium (with 50% Cr), 35% of aluminum and 5% of ammonium chloride served as the chromizing charge, whereas (Bondyuzhskii) carburizer crushed to powder was used as a source of carbon. Surface impregnation of specimens was carried out in heat-resistant crucibles provided with fusible seals for 4.6 and 10 h at 900, 1000 and 1100°C.

From Figs. 108 and 109, it can be seen that the diffusion layers produced by simultaneous surface impregnation of steels with carbon and chromium can be classified into three basic groups: continuous carbide layers ($Cr_{23}C_6$

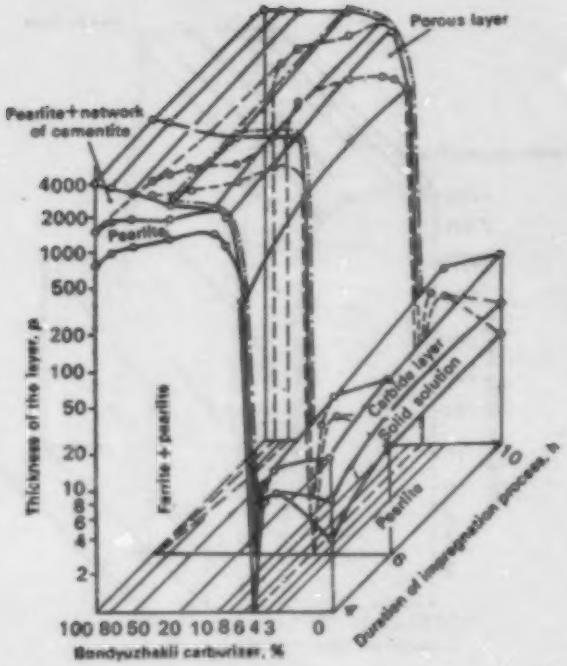

Fig. 108. Variation in phases of diffusion layers with composition of active mixture and duration of treatment (steel 15, $t = 1100$°C).

and Cr_7C_3) with a thin sublayer of solid solution of chromium in iron, ferrite, i.e. a typical chromized coating on steels; carbochromized layers, distinguished from carburized layers by a higher chromium content in the surface layer; and carburized layers with a porous brittle carbide layer on the surface.

Typical chromized layers on the steels under investigation are formed only in mixtures containing up to 4–10 wt.% of Bondyuzhskii carburizer; moreover, the zones of chromized layers on steel 15, steel 40Kh and steel 5KhNV are weakly dependent on the temperature of impregnation and limited by 4% of Bondyuzhskii carburizer in the mixture. In the case of steel ShKh15, the limiting concentration of the carburizing constituent, ensuring the formation of a continuous carbochromized layer, reduces with increasing temperature of impregnation (from 10% at 900°C to 6% at 1100°C). Additions of Bondyuzhskii carburizer cause a slight improvement in the thickness of the carbide layer. However, this effect (increase in thickness of the diffusion layer) is not significant and is not observed on all steels (this has also been experimentally confirmed by Dubinin [101]). Therefore, in our opinion, the introduction of

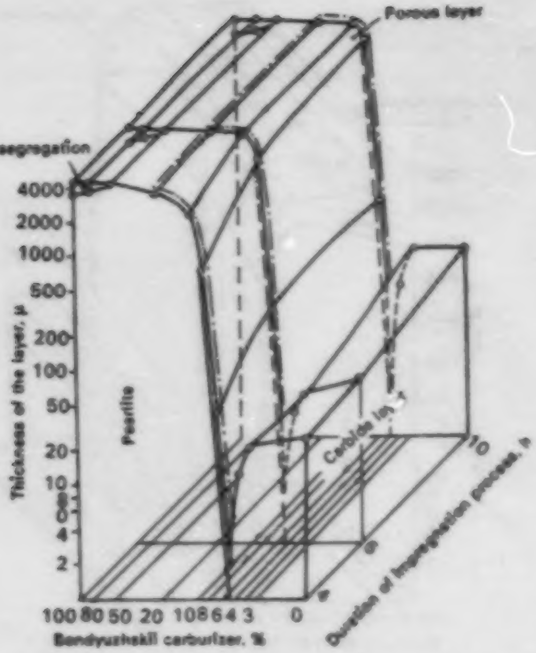

Fig. 109. Variation in phases of diffusion layers with composition of mixture and duration of treatment (steel ShKh15, $t = 1100$°C).

small amounts of carburizer in the chromizing mixture in order to increase the thickness of the carbide layer does not serve any useful purpose.

The carbochromized layer obtained in mixtures containing 20–50% of the chromizing constituent contains up to 2.5 to 5% Cr in the surface zone. The concentration of chromium in the diffusion layer increases with increase in the ferrochromium content of the active mixture and temperature of impregnation.

There is not much difference in the structure of carburized and carbochromized layers, obtained at 900°C, on the steels under investigation (active mixture containing 20–50% of the chromizing constituent). The surface zone of carburized specimens contains a somewhat larger amount of carbides, which is related, probably, to the high carburizing power of Bondyuzhskii carburizer without chromizing additives. The concentration of chromium on the surface of carbochromized steels is not very high (not more than 1.5–2.0%).

An increase in the surface-saturation temperature up to 1000–1100°C considerably accelerates the diffusion, and the concentration of chromium in the surface zone of carbochromized layers increases up to 3–5%. Carbochromized diffusion coatings produced under these conditions are far superior to carburized coatings. Simultaneous diffusion of chromium and carbon leads to the formation of a diffusion layer with a fine-grain structure, significant improvement in the stability of the austenite, absence of coarse cementite particles, precipitation of acicular cementite in pearlite grains and large carbide inclusions in the surface zone of the layer (Fig. 110). The fine carbide network in the carbochromized layer can be eliminated by normalizing, if necessary. The production of such layers is of great practical importance.

Diffusion layers of the third type, the structure of which is shown in Fig. 111, obtained in mixtures containing 6 to 20% of carburizing constituents reveal enhanced porosity and brittleness. They spall easily and will probably not find any industrial application. The thickness of the porous carbide zone increases with increase in temperature and duration of treatment. The thickness of the carburized layer beneath the porous layer also increases simultaneously. The pores in the carbide layer are apparently filled with graphite and ensure a supply of carbon to the surface of the steel.

The formation of a porous carbide layer takes place, probably, due to chemical kinetics. With a considerable excess of carbon the interaction of carbon (or carbon dioxide) formed in the mixture, with the chloride of chromium, results in the formation of carbides of chromium on the surface of the steel substrate. The gaps between the growing crystals of carbides are filled up by the excess carbon.

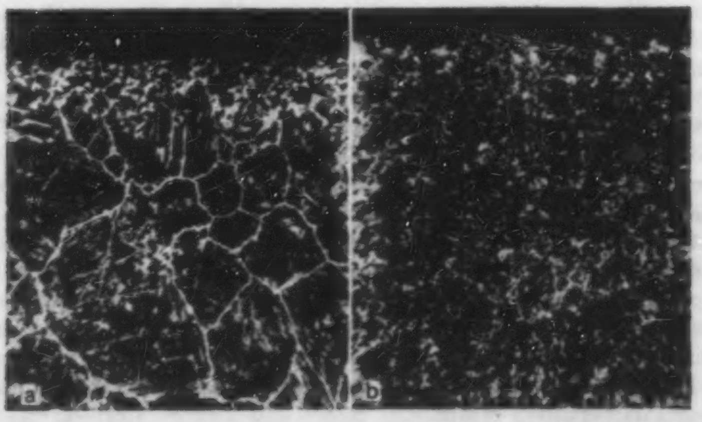

Fig. 110. Microstructures of (a) carburized, (b) carbochromized (obtained in Bondyuzhskii carburizer with 50% chromizing constituent) layers on steel 40Kh: $t = 1000°C$, $\tau = 10$ h.

Fig. 111. Microstructure of porous carbochromized layers on steel ShKh15:

a—8% chromizing constituent; $t=1100°C$, $\tau=6$ h;
b—6% chromizing constituent; $t=1100°C$, $\tau=10$ h.

X-ray diffraction analysis of the surface of the porous zone on the specimens of steels under investigation revealed the presence of carbides, $Cr_{23}C_6$ and Cr_7C_3. The x-ray diffraction pattern adopted on pieces from the surface of sintered chromium-in-iron powder mixture containing 5, 10 and 15% of wood charcoal and sintered at 950°C for 8 h as well as mixtures of similar compositions, to which further additions of ammonium chloride were made, indicated the presence of lines of carbides, $Cr_{23}C_6$ and Cr_7C_3.

Studies on the microhardness of particles in powder mixtures used for surface treatment of steel were carried out on microsections prepared with the help of a self-setting plastic. This established the presence of particles of 30×20 μ with a 1000–1600 kgf/mm^2 microhardness (probably carbides of chromium) in the powder mixture.

The observed phenomenon of formation of a diffusion layer during simultaneous impregnation of steel with carbon and chromium can be explained as follows. At the treatment temperature, atomic carbon (or carbon monoxide) and chlorides of chromium are formed in the carbochromizing mixture. Their interaction with the surface of the steel substrate results in surface saturation of steel with carbon and chromium. At the same time, carbides of chromium are formed in the mixture, their concentration being maximum in mixtures containing 6–20% of Bondyuzhskii carburizer. Nucleation and subsequent growth of carbides of chromium also takes place on the prepared steel substrate surface being saturated and lead to the formation of porous carbide layers through which a supply of carbon to the surface of the steel is maintained (Fig. 111, a). In mixtures containing 6% of Bondyuzhskii carburizer, along with the porous layer a continuous carbide layer may also be formed (Fig. 111, b). The formation of a continuous carbide layer on the surface of the steel hinders its impregnation with carbon.

It thus follows that during carbochromizing in powder mixtures, a high-temperature deposition of carbides of chromium takes place along with surface impregnation of the steel. In the case of a low activity of the process of carbide formation, in mixtures containing up to 6% and more than 20% of Bondyuzhskii carburizer either a continuous carbide diffusion coating or a carburized layer alloyed with chromium is formed on the surface of the steel. Studies on the feasibility of producing impervious carbide layers of adequate thickness by deposition of carbides of chromium on the surface of steel will be of great practical importance.

A unique method of carbochromizing in powder mixtures has been developed by Malinav et al. [358] and Vanitskii et al. [366]. For surface impregnation, a powder mixture of chromium (or ferrochromium), aluminum oxide and ammonium chloride was used. In contrast to the normal powder method, in this case a low-melting component of gray cast-iron powder is introduced in the active mixture. At temperatures above 1200°C, cast-iron powder in contact with the surface of the metal substrate melts forming an envelope of liquid phase around the component. The fraction of cast iron in the powder mixture should be about 30–40%. This liquid envelope, itself saturated with chromium from the powder mixture, becomes the coating, on solidification. The structure of such a coating corresponds to that observed in cast ledeburite alloys. The thickness of the diffusion coating obtained on plain carbon and low-alloy steels were found to be 0.2–0.6 mm thick. The surface-alloyed layer contained approximately 3% of C and 15–60% of Cr. This new method of diffusion coating is not only suitable for the protection of new components from wear and corrosion but can also be successfully used for restoration of worn-out components.

Kulyba and Reva [361] have studied the feasibility of producing chromized and titanized coatings on steel and cast iron by reducing the pressure of the dissociated carbon tetrachloride ambient. Powders of chromium and titanium were used as sources of diffusing agents in the active gaseous medium.

During heating the reaction chamber was continuously evacuated using a forepump in order to ensure oxygen-free atmosphere. At 800°C and a pressure in the reaction chamber of approximately 10^{-1} mmHg, the pump was switched off and the working volume in the chamber was filled with vapors of carbon tetrachloride to a residual pressure of 10–20 mmHg. Surface impregnation was carried out for 5 h at 1000°C. At the treatment temperature, carbon-tetrachloride vapors dissociated into carbon and chlorine which interacted with the powders of the alloying elements, e.g. chromium (titanium). As a result, an active gaseous phase was formed inside the reaction chamber.

The formation of active atoms of carbon and chlorides of chromium (titanium) in the container leads to a simultaneous diffusion saturation of the surface of steels and cast iron with carbon and chromium.

Carbochromized and titanized diffusion layers were obtained by introducing small quantities of carbon tetrachloride in the reaction chamber. On plain carbon steels, the carbide layer is well bonded with the substrate metal, and there is no decarburized zone beneath the carbide layer. This phenomenon has been attributed by the authors of [361] to a simultaneous diffusion of chromium and carbon in the surface layer of steel.

Introduction of larger quantities of carbon tetrachloride, according to the authors of [361], leads to pitting on the specimens. The structure of the layers obtained (see [361]), under these conditions has not been investigated. It can be assumed that, on introduction of large quantities of carbon tetrachloride, a porous brittle carbide layer is formed on the surface which chips off easily. Unfortunately, in this investigation, the feasibility of producing carburized layers, alloyed with chromium, has not been studied.

Successive surface saturation of steels with carbon and chromium results in the formation of carburized layers with a comparatively thin (a few tens of microns) carbide layer on the surface and a high hardness and wear-resistance.

Successive carbochromizing results in a 5 to 10% improvement in the yield strengths of steel 20, steel 45, steel 3Kh2V8F and steel 4Kh5V2FC, a reduction in ductility and improvement in their resistance to fatigue and corrosion [355, 360]. As in the case of chromizing, successive diffusion saturation of steels 3Kh2V8F and 4Kh5V2FC with carbon and chromium ensures a good resistance to the action of liquid aluminum alloy Al2 at 700°C and also resistance to oxidation in air at 1000°C [355].

Results of measurement of hardness of steel 15, steel ShKh15, steel 40Kh and steel 5KhNV, impregnated simultaneously with carbon and chromium for 10 h at 900 and 1000°C, in a powder mixture containing ferrochromium, oxide of aluminum and ammonium chloride with Bondyuzhskii carburizer, and oil quenched from 840°C are reproduced in Table 77.

In all the specimens of carbochromized steels, the hardness measured after tempering was found to be higher than that obtained for carburized specimens. The maximum hardness was that of specimens carbochromized in mixtures containing 50 and 80 wt.% of Bondyuzhskii carburizer. In such cases, the surface layer contained 3–5% of Cr.

Table 77

Content of Bondyuzhskii carburizer in active mixture, wt.%	Treatment temperature, °C	Hardness, HRC			
		steel 15	steel ShKh15	steel 40Kh	steel 5KhNV
100	900	62–63	63–64	64	59
	1000	61	61	64	60
80	900	63–64	65–66	64–65	61–62
	1000	63–64	65–66	—	61
50	900	65–66	64–65	64–65	61–62
	1000	65	65–66	64–66	—
20	900	59	64–65	64–65	62–63
	1000	64	64–65	—	60–61

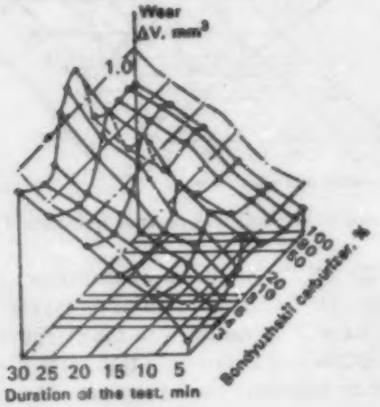

Fig. 112. Results of investigations on wear resistance of carbochromized steel ShKh15.

The results of studies on wear resistance of specimens of steel ShKh15 and steel 5KhNV, surface alloyed at 1100°C for 10 h, quenched from 840°C and tempered at 200°C, are given in Figs. 112 and 113. Broken lines represent the rate of wear of the same steels after hardening and tempering at low temperature. Similar plots are shown for steel 15 and steel 40Kh.

The maximum wear resistance was that of a continuous carbochromized coating; somewhat lower values are obtained for carburized and carbochromized coatings, obtained with a mixture containing 20–80% of Bondyuzhskii carburizer.

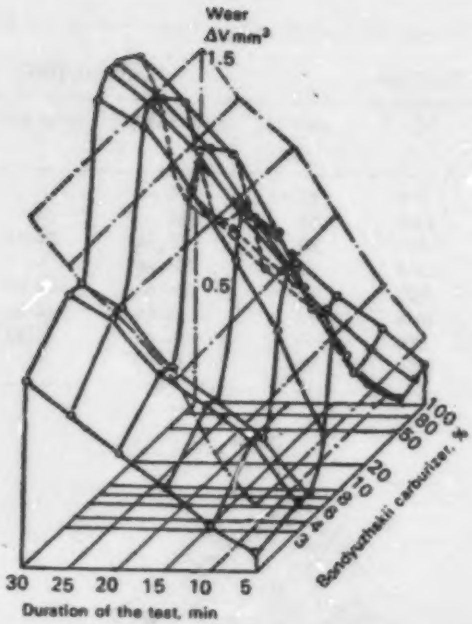

Fig. 113. Results of investigations on wear resistance of steel 5KhNV.

Introduction of 20–50% of chromizing constituents in Bondyuzhskii carburizer improves the wear resistance of diffusion layers. The minimum wear resistance (peak on the plot of variation in the extent of wear with composition of the active mixture and duration of testing) is observed in a diffusion layer with a porous carbide zone on the surface. The maximum wear resistance is noted in continuous chromized layers on steel 5KhNV, somewhat lower values were observed for diffusion coatings on steel 40Kh and steel ShKh15 and the minimum wear was observed on diffusion coated steel 15. Based on the wear resistance of carbochromized layers (content of Bondyuzhskii carburizer in the active mixture 50–80%) the investigated steels can be placed in the order of decreasing wear resistance as follows: steel ShKh15, steel 40Kh, steel 15, and steel 5KhNV. A lower wear resistance of carbochromized steel 5KhNV, as compared to other steels investigated, is probably related to the fairly high residual content of austenite in the diffusion layer. The wear resistance of a porous carbochromized layer also decreases in the same order (from steel ShKh15 to 5KhNV).

CHAPTER V

Three-component Diffusion Coatings

Introduction of a third element in the active mixture significantly alters the kinetics of formation of the constituent phases and properties of diffusion layers, and considerably widens the scope of thermochemical treatment. For example, as shown earlier, it is not possible to carry out multicomponent impregnation of steels and alloys with boron and chromium using their powder mixtures, but the introduction of aluminum in the mixture leads to the formation of a diffusion layer, containing all the three elements—boron, chromium and aluminum. Addition of fast-diffusion elements (Al, Si, etc.) in the mixture increases the rate of formation of a three-component diffusion layer as compared to a two-component layers which do not contain the elements indicated above.

Three-component diffusion layers quite often display superior properties as compared to corresponding two-component layers. For example, they, as a rule, have a higher thermal stability [1]. The ever-increasing interest in multicomponent coatings, especially in recent years, is therefore, quite understandable. Unfortunately, scientific investigations in this direction are lagging behind the requirements of industrial production. In our view, this is due to a number of observed factors, the first of these being the unsuitability (to be precise—a low effectiveness) of the conventional approach for the production of diffusion coatings of this type. On increasing the number of impregnating elements up to four and above, far more experimental investigations become necessary. A comprehensive and systematic study of the properties of diffusion coatings as a function of technological parameters of the process as well as of the composition of mixture, in a conventional manner, is, generally, beyond the capacity of even large organizations with considerable material and human resources.

Chemical, phase and structural analyses of multicomponent coatings are substantially laborious and methodologically difficult.

From the above, in our view, for the production of multicomponent coatings, it is expedient to use a new methodological approach such as statistical planning and evaluation of experiments, especially with combinatorical methods.

Presently two methods are used for the production of multicomponent diffusion coatings: 1) impregnation in powders of elements or their ferroalloys with additions of activators and 2) an aluminothermic method (impregnation in powders of oxides). This can also be achieved by using a slip-wash method of obtaining the coating, by thermochemical treatment using pastes and by impregnation in metallic baths with additions of the corresponding elements.

Diffusion coating by the powder process is carried out in hermetically sealed containers, preference being accorded to containers provided with fusible seals.

Information and data, available in the literature and to the authors on the technology of production, the kinetics of formation and the properties of a few three-component diffusion coatings are given below.

1. CHROMOALUMINOSILICONIZING*

Simultaneous diffusion saturation of metals and alloys with chromium, aluminum and silicon is employed for the treatment of components subjected to high temperatures such as valve assemblies and turbine blades of engines, heat pipes, combustion chambers, furnace hearths, crucibles, etc. This method can also be used for improving the corrosion resistance of metals and alloys in a number of aggressive mediums.

As a rule, the powder method is used for the production of chromoaluminosiliconized diffusion coatings [1, 101, 272, 301]. For impregnation, a mixture mainly consisting of pure elements (these can be replaced by the corresponding ferroalloys) with additions of aluminum oxide and ammonium chloride is used. According to Dubinin [101] better results are obtained when alloys are treated in mixtures containing 10% of aluminum and up to 10% of silicon. Tarasyuk et al. have used the following system with a different composition of the mixture.

The aggregate concentration of three impregnating elements was 50% of the mixture. Moreover, the concentration of one of these was kept constant, in every series of experiments, and those of the other two were varied by 5–10%. The remaining 50% of the mixture consisted of aluminum oxide (45%) and ammonium chloride (5%). Diffusion coating was carried out for 5 h at 850°C in containers provided with fusible seals. The results of experimental investigations have shown that for surface coatings of ZhS6K alloy, an aluminum-base mixture containing small quantities of silicon and chromium are most suitable.

In our investigations we have used an aluminothermic method for the production of chromoaluminosiliconized diffusion coatings. Oxides of chromium and silicon were used as sources of chromium and silicon, whereas aluminum simultaneously acted as a reducer as well as a diffusant.

*The process of impregnation of metals and alloys with Cr–Al–Si is known as chromoaluminosiliconizing according to the terminology of Dubinin [101]. However, in the works of Zemskov and others it is referred to as aluminochromosiliconizing.

The effect of the aluminum content in the charge (optimum for chromosiliconizing) at constant concentrations of ballast additions and activator (AlF_3) on the formation of chromoaluminosiliconized diffusion coatings is shown in Fig. 114.

The increase in aluminum content of the mixture is accompanied by an increase in the thickness of the diffusion layer. At aluminum concentrations above 40% a preferred aluminizing is observed.

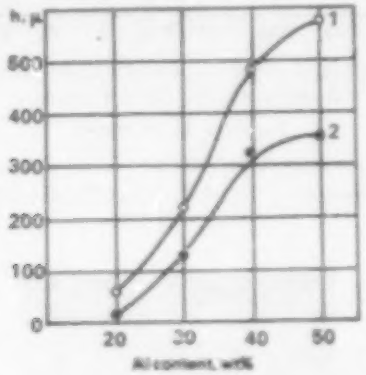

Fig. 114. Effect of concentration of aluminum in a charge on thickness of chromoaluminosiliconized layers on (1) iron and (2) steel U8:

95% {30% Al_2O_3 + 70% [n% Al + (100 − n)% (85% Cr_2O_3 + 15% SiO_2)]} + 5% AlF_3 ($t = 1100$°C, $\tau = 4$ h).

A mixture of the following composition can be recommended for practical application (wt.%):

$$95\%\ \{30\%\ Al_2O_3 + 70\%\ [30\text{–}40\%\ Al + 70\text{–}60\%\ (85\%\ Cr_2O_3 + 15\%\ SiO_2)]\} + 5\%\ AlF_3.$$

The effect of the temperature and duration of impregnation in mixtures containing 30% of aluminum is shown in Fig. 115. As can be seen from the given data, the rate of growth of the diffusion layer during chromoaluminosiliconizing follows neither an exponential nor a parabolic law.

The typical microstructures of diffusion layers on iron and steel are shown in Fig. 116. On commercial iron, during chromoaluminosiliconizing an ordered solid solution of Fe_3Si alloyed with chromium and aluminum, with a microhardness of 645–616 kgf/mm², is formed at the surface. Fe_3Si phase is isomorphous with the chemical compound, Cr_3Si, and the superlattices, FeAl and Fe_3Al, the latter being located just below the α'-phase and alloyed with chromium and silicon.

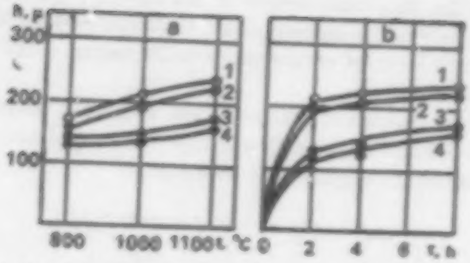

Fig. 115. Effect of temperature and duration of treatment on thickness of chromoaluminosiliconized diffusion coatings:

a—$\tau = 8$ h; b—$t = 1100$°C.

1—Armco iron; 2—steel 20; 3—steel 45; 4—steel U8.

Composition of mixture: 95% (40% Al_2O_3 + 60% [30% Al + 70% (85% Cr_2O_3 + 15% SiO_2)]) + 5% AlF_3.

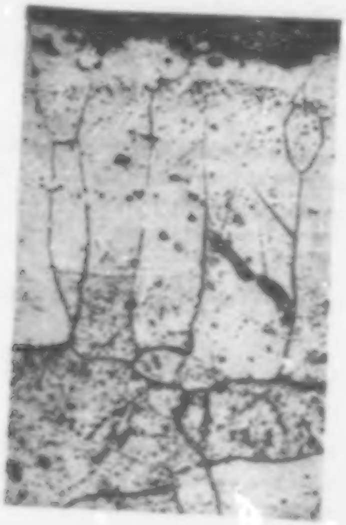

Fig. 116. Microstructure of chromoaluminosiliconized coating on iron, ×200.

Finely dispersed particles of $(Fe, Cr)_3Si$ precipitated from supersaturated solid solution during slow cooling during the treatment temperature are observed in the zone of ordered solid solution of FeAl close to Fe_3Si.

The superlattice of Fe_3Al is converted to a disordered solution of aluminum, chromium and silicon in α-iron. The zone of solid solutions

(FeAl–α-phase) has a variable microhardness, gradually decreasing across the depth of the layer from 485 to 190 kgf/mm^2.

On plain carbon steels (steel 45) and steel U8, carbide $(Cr, Fe)_7C_3$, with a microhardness of 1315–1225 kgf/mm^2 is formed at the surface, beneath which are located superlattice structures of FeAl and Fe_3Al; the latter transforms to a disordered α-phase. Precipitation of $(Fe, Cr)_3Si$ is observed in the zone of FeAl. The zone of solid solution has a microhardness in the range of 395–220 kgf/mm^2.

Concentrations of chromium, aluminum and silicon in the surface layer of steel 45 are found to reach 36.7, 2.3 and 3.55%, respectively.

Carbon hampers the rate of formation of chromoaluminosiliconized layers on steels. Nickel and chromium also have a similar effect, whereas molybdenum, titanium and, especially, silicon increase the thickness of the diffusion layer. The thicknesses of surface diffusion layers on some special steels are given in Tables 78 and 79.

G.V. Zemskov [21] has obtained interesting data on the kinetics of formation of chromoaluminosiliconized diffusion layers on ZhS6k alloy.

An increase in the chromium content of the charge reduces the thickness

Table 78

Base metal (steel)	Thickness of chromoaluminosiliconized layer, μ (1100°C, 8 h)
40	245
40Kh	210
40Kh2	210
40Kh3	210
40Kh5	210
40M (0, 6)	240
40M (1, 1)	245
40N2	140
40N3	110
40N5	110
40S	245
40S3	365
40S4	520
40T (0, 4)	280
20Kh3MVF	220
2Kh13	510
Kh25T	20
1Kh18N9T	105
3Kh19NMVBT	140
EI-867	90

Table 79

Material	Wt. gain, g/m² at 1000°C, 26 h				
	untreated base metal	Cr–Si	Si–Al	Cr–Al	Cr–Al–Si
Armco iron	1454	98	15.3	28	22.0
Steel 20	1310	97	16.0	27	44.9
Steel 45	1395	79	15.7	34	31.8
Steel 48	1100	53	17.5	31	49.8

as well as the microhardness of the diffusion layer (Fig. 117). An increase in silicon content leads to a coarsening of the diffusion layer and reduce its thickness. At 80% of Si, a minimum is observed on the plot of thickness of the diffusion layer versus composition of the active mixture, which is related to the fall in potential of the diffusion source and, possibly, to the concentration dependence of the coefficients of diffusion. The microhardness of the surface layer with minimum thickness was found to be 650–750 kgf/mm²; in other cases it was from 800–900 kgf/mm² (Fig. 117).

The diffusion layers obtained are distinguishable from those obtained by aluminizing (with respect to microstructure) only in cases where the mixture contains large amounts of chromium and silicon.

For practical applications, as indicated earlier, mixtures containing smaller amounts of chromium and silicon should be preferred.

As can be observed by x-ray structure analysis, on chromoaluminosiliconizing (using the optimum composition of the active mixture) the predominant phase in the surface layer is Ni_2Al_3. Concentrations of alloying elements in the diffusion layer have been determined by chemical analysis (Fig. 118). In the surface zone of a thickness of 40–60 μ, the concentration of aluminum remains constant at 45–50%. Silicon has been traced to a depth of 60 μ, its concentration being approximately 3%. The concentration of nickel in the surface layer ranges between 50–40%.

Chromoaluminosiliconizing provides a fairly reliable protection from oxidation to plain carbon as well as alloy steels. The heat resistance of plain carbon steels at 1000°C is found to improve by 20 to 65 times as compared to that of the untreated state (Table 79). For purposes of comparison, in Fig. 79, the data for the corresponding two-component diffusion coatings has also been included. Although increase in heat resistance in short-duration testing of chromoaluminosiliconized diffusion coatings is found to be somewhat lower than that of silicoaluminized coatings, under conditions of long-term application they are in no way less reliable than the latter.

The average improvement in heat resistance of stainless and high-temperature creep-resistant steels after chromoaluminosiliconizing, is found to be

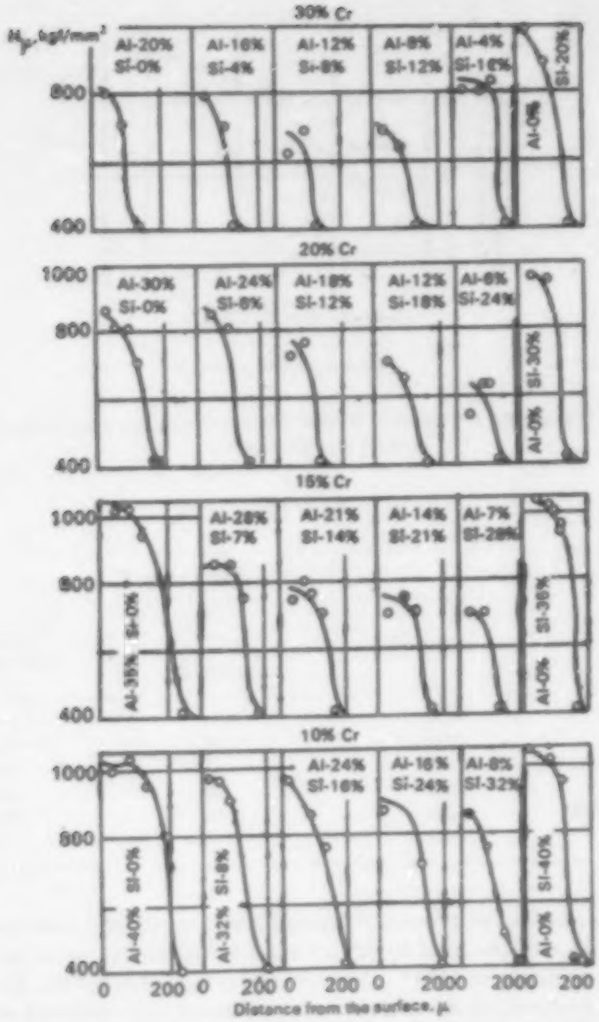

Fig. 117. Microhardness of chromoaluminosiliconized coatings on ZhS6K alloy.

from 4 to 6 times (Table 80). Chromoaluminosiliconizing of EI-867 alloy does not protect it from high-temperature gas corrosion.

The high heat resistance of steels is attributed to the strength, density and continuity of the oxide layer formed and to the resistance of the chromoaluminosiliconized coating to thermal fatigue [101].

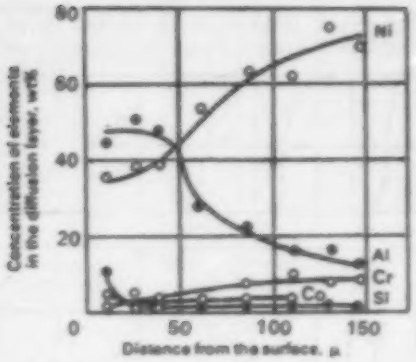

Fig. 118. Distribution of elements in diffusion-saturated chromoaluminosiliconized layer on ZhS6K alloy.

Table 80

Base metal	Wt. gain, g/m² at 1000°C		
	untreated	Cr–Al–Si diffusion coating	duration of test, h
20Kh3MVF	4742	1230	100
2Kh13	1480	11	100
Kh25T	45	43	100
Kh18N9T	205	32	150
3Kh19N9MVBT	240	66	100
EI-867	26.5	33.4	150

The chromoaluminosiliconized layer obtained in mixtures containing not more than 20–25% (each) of chromium and silicon, reliably protects ZhS6K alloy from oxidation at 1100°C (duration of test $t_{test} = 200$ h) [28]. The maximum heat resistance is that of the coating obtained in a mixture containing small additions of chromium and silicon (up to 10–15% of each). Specimens processed in these active mixtures, indicated a minimum weight gain (20–30% less than that for aluminized specimens) and Ni_3Al phase, which has a very low heat resistance, was not observed in their microstructures.

General Motors have carried out tests on chromoaluminosiliconized and other diffusion coatings on Hastalloy x at 1150°C using a velocity of gas flow of 610 m/s. The results of tests, carried out for 2 h, are given in Table 81.

Table 81

Coating on Hastalloy	Depth of erosion, mm
Untreated	0.16
Al	0.07
Al–Cr	0.06
Al–Si	0.05
Cr–Al–Si	0.03

Chromoaluminosiliconized diffusion coatings have been recommended for improving the erosion resistance of thermo-couple sheaths used for determination of temperature in the inlet assembly of turbines.

Other specimens (in the form of blades) were tested for thermal fatigue. Specimens along with special gadgets were rotated at a speed of 1725 rpm. The parameters of thermal cycling were as follows: heating to 1150°C in 1 min and cooling to 150°C in 1.5 min. The results were satisfactory.

In England turbine blades (made of molybdenum) used in the engine of the "Rotodyne" aircraft are subjected to chromoaluminosiliconizing. The temperature at the edges of these blades is known to reach 1500–1600°C [272].

Chromoaluminosiliconizing reliably protects medium and high-carbon steels from corrosion in dilute nitric acid. A significant improvement in corrosion resistance in sodium chloride solution is observed after chromoaluminosiliconizing. However, chromoaluminosiliconizing fails to protect against the corrosive action of sulfuric, hydrochloric, phosphoric and acetic acids.

2. CHROMOTITANOALUMINIZING

Simultaneous diffusion saturation of metals and alloys with chromium, titanium and aluminum can be employed to improve heat and corrosion resistance in different corrosive mediums.

Only one method of chromotitanoaluminizing, i.e. the aluminothermic method, has been well studied. Oxides of chromium and titanium are used as the source of active atoms in aluminothermic mixtures. The source of active atoms of aluminum is pure aluminum, which is introduced in the active mixture in quantities larger than those required for the complete reduction of Cr_2O_3 and TiO_2. It is obvious that a diffusion layer can be produced by using pure metals. Taking them in requisite proportions, suitable results can be obtained. However, from the point of view of economy the aluminothermic process is much more effective. The effect of the ratio of oxides of titanium and chromium at constant concentrations of aluminum, ballast addition (Al_2O_3) and activator (AlF_3), on the formation of chromotitanoaluminized coatings is shown in Fig. 119.

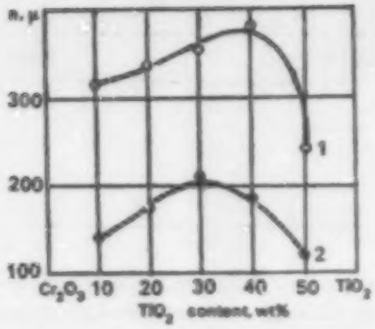

Fig. 119. Dependence of thickness of chromotitanoaluminized coatings on (1) iron and (2) steel 20 on ratio of TiO_2 and Cr_2O_3 in a mixture containing 35% Al, 40% Al_2O_3 and 5% AlF_3.

On increasing the concentration of titanium dioxide and reducing the concentration of chromic oxide in the mixture, the thickness of the diffusion layer increases and at 30–40% of TiO_2 in the charge, a maximum is observed on the plot of thickness of the coating versus composition of the active mixture. A further rise in the titanium content of the charge is accompanied by a reduction in thickness of the diffusion layer on iron as well as on steel U8. The latter can, most probably, be explained by the formation of the chemical compound, Cr_3Ti, in the mixture and partly in the diffusion layer.

The effect of the technological parameters of treatment and the composition of the active mixture on the thickness of a chromotitanoaluminized coating is shown in Table 82.

The selection of the optimum composition is based on the kinetics of formation of the diffusion layer as well as on the characteristics of the layer produced, especially its heat resistance.

The effect of the ratio of chromic oxide and titanium dioxide and concentration of aluminum in the mixture on the oxidation resistance of the coating obtained is shown in Fig. 120. For practical applications, the following composition of the active mixture is considered optimum:

$$95\%\,\{40\%\,Al_2O_3 + 60\%\,[45\%\,Al + 55\%\,(70\%\,Cr_2O_3 + 30\%\,TiO_2)]\} + 5\%\,AlF_3.$$

The effect of the temperature and duration of treatment (using an active mixture of optimum composition as given above) on the thickness of a chromotitanoaluminized layer is shown in Fig. 121.

From the given data, it can be seen that neither the exponential nor the parabolic law of growth of a diffusion layer is applicable in the present case.

Table 82

Composition of mixture, wt.% [A Al_2O_3 + (100 − A) [x Al + (100 − x) (y Cr_2O_3 + z TiO_2)] + n AlF_3					Treatment parameters		Aggregate thickness of chromotitanoaluminized layer, μ			
							base material			
Al_2O_3	Al	Cr_2O_3	TiO_2	AlF_3	t, °C	τ, h	Commercial iron	steel 20	steel 45	steel U8
40	35	90	10	5	1100	4	315	315	180	140
40	35	80	20	5	1100	4	335	335	210	175
40	35	70	30	5	1100	4	350	350	250	210
40	35	60	40	5	1100	4	385	385	210	175
40	35	50	50	5	1100	4	245	230	140	120
40	45	70	30	5	1100	4	350	340	280	230
40	35	70	30	5	1100	8	350	350	250	225
40	35	60	40	5	1100	8	470	445	245	210
40	35	50	50	5	1100	8	385	350	245	190
40	45	70	30	5	1100	8	665	630	580	560
40	45	50	50	5	1100	8	420	380	315	265
40	45	70	30	5	900	2	70	65	45	40
40	45	70	30	5	900	4	140	125	110	85
40	45	70	30	5	900	8	175	160	140	100
40	45	70	30	5	1000	2	175	170	155	110
40	45	70	30	5	1000	4	280	265	195	150
40	45	70	30	5	1000	8	350	315	280	210
40	45	70	30	5	1100	2	315	280	240	175
40	45	70	30	5	1100	4	350	340	280	230
40	45	70	30	5	1100	8	665	630	580	535

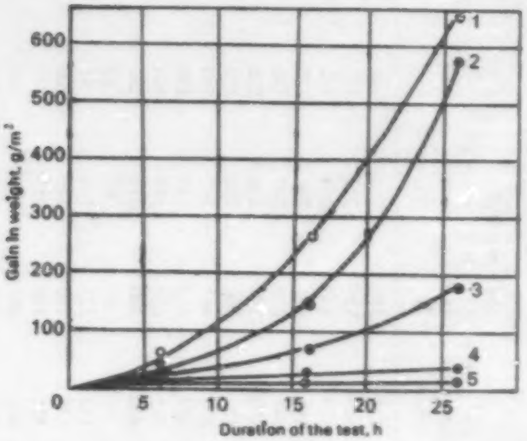

Fig. 120. Effect of ratio of Cr_2O_3 and TiO_2 and concentration of aluminum in a charge on heat resistance of a chromotitanoaluminized layer on steel 45:

1—$\frac{Cr_2O_3}{TiO_2}=\frac{50\%}{50\%}$, Al—35%; 2—$\frac{Cr_2O_3}{TiO_2}=\frac{60\%}{40\%}$, Al—35%; 3—$\frac{Cr_2O_3}{TiO_2}=\frac{70\%}{30\%}$, Al—35%;
4—$\frac{Cr_2O_3}{TiO_2}=\frac{50\%}{50\%}$, Al—45%; 5—$\frac{Cr_2O_3}{TiO_2}=\frac{70\%}{30\%}$, Al—45%, $t=1000°C$.

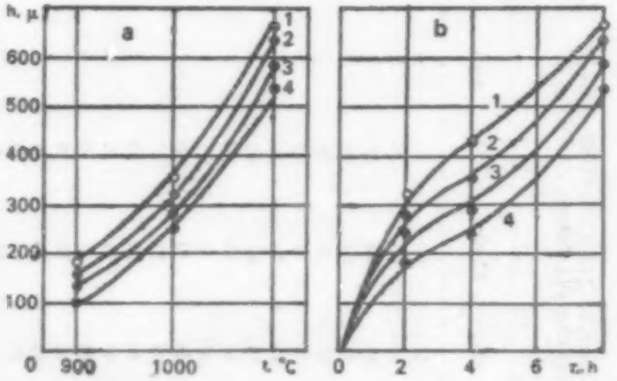

Fig. 121. Effect of temperature and duration of treatment on the thickness of a chromotitanoaluminized layer on (1) Armco iron, (2) steel 20, (3) steel 45 and (4) steel U8:

a—$\tau=8$ h; b—$t=1100°C$.

Mixture composition: 95% {40% Al_2O_3 + 60% [n% Al + (100–n)% (70% Cr_2O_3 + 30% TiO_2)]} + 5% AlF_3.

The latter, as pointed out earlier, seems to be the rule rather than the exception in the case of multicomponent coatings.

Identical phases are formed in the chromotitanoaluminized layer on iron and plain carbon steels, produced by an aluminothermic process (the difference observed is of a purely quantitative nature). Aluminide—Fe_2Al_5 is formed at the surface of the component being treated and a precipitate of the chemical compound, Cr_2Ti, is observed in this zone. The surface hardness increases with the carbon content—from 680 on commercial iron to 735 kgf/mm^2 on steel U8. Across the thickness of the phase it gradually decreases to 635 kgf/mm^2. The zone of the superlattices, FeAl and Fe_3Al, alloyed with chromium and titanium, with finely dispersed precipitates of Cr_2Ti, is located beneath the aluminide, Fe_2Al_5. A disordered solid solution of all the three elements in α-iron adjoins the base metal (Fig. 122). The zone of solid solutions (including superlattices) has a variable microhardness, gradually decreasing in the direction of the core from 555 to 190 kgf/mm^2.

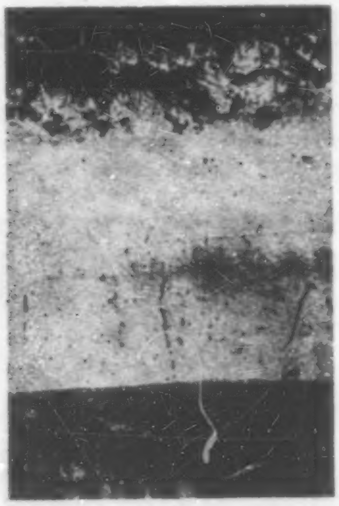

Fig. 122. Microstructure of chromotitanoaluminized layer on steel 45.

The concentration of aluminum, chromium and titanium on the surface of chromotitanoaluminized steel 45 is found to be 47.4, 0.4 and 0.2%, respectively. Carbon hampers the rate of formation of chromotitanoaluminized coatings (Fig. 123).

Silicon and titanium in medium carbon steels (0.04% C) increase the thickness of the diffusion layer; chromium when present in small quantities (up to

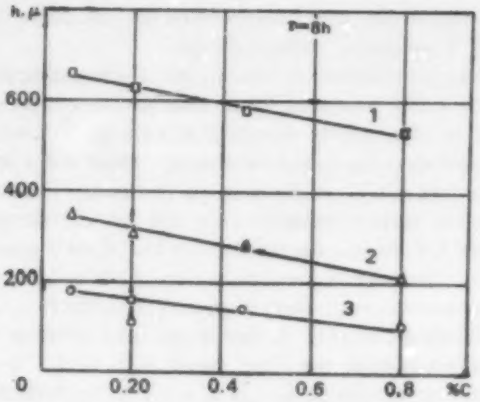

Fig. 123. Effect of carbon concentration on thickness of Cr–Ti–Al coating: t = 1—1100°C; 2—1000°C; 3—900°C.

5%) has hardly any effect, whereas molybdenum and, especially, nickel reduce the thickness of surface-impregnated coatings. The introduction of higer concentrations of chromium (13% and above) in steels also results in a sharp reduction in the rate of formation of the coating. Similar results are obtained in complex alloying of steel with many elements. The microstructure of the diffusion layer on steel 40Kh5 is shown in Fig. 124.

Fig. 124. Microstructure of diffusion-saturated Cr–Ti–Al layer on steel 40Kh5.

The mechanical properties of chromotitanoaluminized medium carbon steels in the normalized state after subsequent tempering is somewhat inferior to the same metal which has not been subjected to thermochemical treatment (Table 83).

Table 83

Mechanical properties	Steel 45 normalized and tempered	Steel 45, chromotitanoaluminized and heat treated
σ_B, kgf/mm^2	75.0	69.5
δ, %	12.6	7.1
ψ, %	65.0	31.3
a_H, kgm/cm^2	15.5	9.3

The strength of steel 45 in the tempered state resulting from chromotitanoaluminizing is found to deteriorate by 8–10%.

From Table 84 it can be seen that chromotitanoaluminized coatings on plain carbon steels significantly improve their heat resistance at 1000°C. This mode of thermochemical treatment increases the heat resistance of alloy steels and high-temperature creep-resistant alloys (Table 85).

Table 84

Material	Wt. gain, g/m^2 at 1000°C duration of test, 26 h	
	untreated state	after chromotitanoaluminizing
Commercial iron	1454	8.5
Steel 20	1310	9.57
Steel 45	1395	7.35
Steel U8	1100	10.7

Note: Treatment parameters: $t=1100$°C, $\tau=8$ h.

Table 85

Material	Duration of test, h	Wt. gain at 1000°C, g/m^2	
		untreated material	Cr–Ti–Al coating
Steel 40	26	1350	12.6
20Kh3MVF	1000	4742	139
2Kh13	100	1480	19.0
Kh25T	100	45	40.5
Kh18N9T	150	205	44.0
3Kh19N9MVBT	100	240	68.5
Alloy EI-867	150	26.5	17.0

Except in 10% dilute nitric acid, a chromotitanoaluminized coating does not protect steels from corrosion damage in most of the investigated mediums (Table 86).

3. TITANOALUMINOSILICONIZING

Simultaneous diffusion saturation of steels with titanium, aluminum and chromium improves their resistance to heat and corrosion in various corrosive mediums.

Titanoaluminosiliconizing can be carried out in powder mixtures of pure metals or their ferroalloys and also in powders of their oxides (aluminothermic process).

In the latter case, the oxides of titanium and silicon are the sources of active atoms. The effects of the parameters of treatment on the thickness of titanoaluminosiliconized coatings are shown in Fig. 125.

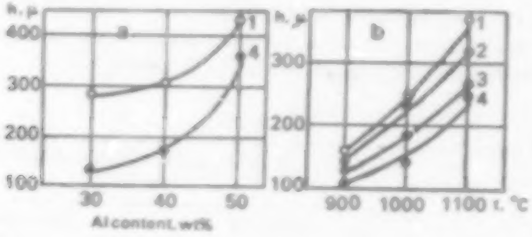

Fig. 125. Effects of parameters of treatment on thickness of titanoaluminosiliconized coatings (1—Armco iron; 2—steel 20; 3—steel 45; 4—steel U8).

a—$t = 1100°C$, $\tau = 4$ h:

Composition of mixture: 95% {40% Al_2O_3 + 60% [40% Al + 60% (85% TiO_2 + 15% SiO_2)]} + 5% AlF_3; $\tau = 8$ h.

An increase in the aluminum content of the active mixture is accompanied by an increase in the thickness of the diffusion layer; further, at aluminum concentrations in the mixture of 40% and above, a preferred aluminizing of the surface is observed.

An active mixture of the following composition can be recommended as most suitable for titanoaluminosiliconizing of steels:

$$95\%\ \{40\%\ Al_2O_3 + 60\%\ [30\text{–}40\%\ Al + 70\text{–}60\%\ (85\%\ TiO_2 + 15\%\ SiO_2)]\} + 5\%\ AlF_3.$$

Increasing the concentration of carbon in steel considerably retards the rate of formation of the diffusion layer (Fig. 126).

Table 86

Testing medium	Wt. loss, g/m² for 75 h							
	untreated				Cr–Ti–Al coating			
	commercial iron	steel 20	steel 45	steel U8	commercial iron	steel 20	steel 45	steel U8
3% NaCl	11.6	5.2	4.5	8.7	9.0	6.0	3.0	9.0
10% H_2SO_4	32	76	832	1200	2000	1940	2330	1450
30% HCl	592	1766	3543	1389	1846	2619	2500	2600
40% H_3PO_4	43	113	1192	1173	1548	2080	2163	1817
10% HNO_3	6128	5748	6070	5720	4.5	7.0	9.0	4.5
50% CH_3COOH	42	39	44	42	9.0	14.0	69	25

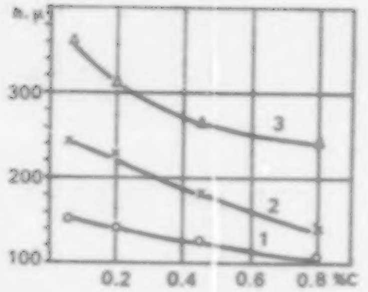

Fig. 126. Effect of concentration of carbon in steel on thickness of Ti–Al–Si coating

Temperature: 1—900°C; 2—1000°C; 3—1100°C.

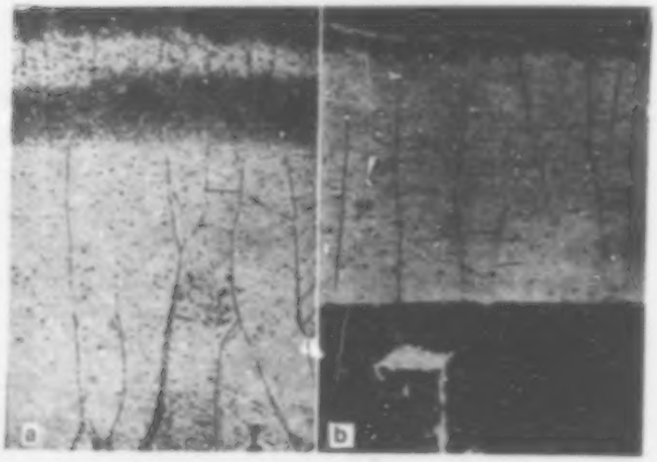

Fig. 127. Microstructure of titanoaluminosiliconized coating on (a) iron and (b) steel 45.

Typical structures of titanoaluminosiliconized coatings on iron and steel 45 are shown in Fig. 127.

Fe_2Al_5, alloyed with titanium and chromium (microhardness 680–650 kgf/mm^2) forms at the surface of titanoaluminosiliconized iron. Inclusions are observed in the aluminide of iron, Ti_5Si_3 (isomorphous with Fe_5Si_3). The microhardness of the silicide, Ti_5Si_3, is 1100–1000 kgf/mm^2.

Superlattices of FeAl and Fe_3Al alloyed with titanium and silicon are located beneath the siliconized layer. On slow cooling from the temperature of impregnation, precipitation of finely dispersed Ti_5Si_3 takes place in the matrix of superlattices, which increases its strength. The α-phase, with a typical acicular structure, is located at the interface with the base metal. The microhardness of solid solutions (including superlattices) decreases from 530 to 180 kgf/mm².

Carbides, (Ti, Fe)C, are formed on the surface of plain carbon steels, steel 45 and steel U8. The concentration of titanium is 52% and the microhardness is of 1890–1780 kgf/mm².

Identical phases, distributed in a similar manner as coatings on Armco iron, are formed below the carbide layer on plain carbon steels. The only difference is the somewhat higher hardness of aluminide Fe_2Al_5 (710–635 kgf/mm²) and α-solid solution adjoining the base metal (220 instead of 180 kgf/mm²). The concentrations of aluminum, chromium and titanium in Fe_2Al_5 are up to 41.0, 10.0 and 12.9%, respectively.

Titanoaluminosiliconized plain carbon steels have a high resistance to oxidation (Table 87).

Table 87

Material	Wt. gain, g/m² at 1000°C for 26 h	
	untreated	Ti–Al–Si coated
Armco iron	1454	30.1
Steel 20	1310	35.4
Steel 45	1395	52.0
Steel U8	1100	49.0

The results of short-duration tests at 1000°C show a 20 to 40 fold improvement in oxidation resistance of titanoaluminosiliconized steels. This is comparable with the heat resistance of the best two-component coatings. However, in the case of long-term exposures, three-component coatings should be preferred, as the rate of diffusion resorption of the latter, at working temperatures, is considerably lower than that for two-component coatings.

Titanoaluminosiliconizing reduces the rate of distintegration of low-carbon steels by corrosion in sea water and that of high-carbon steels in dilute hydrochloric and acetic acids. A notable increase in the corrosion resistance of Ti–Al–Si coated carbon steels is observed in nitric acid—from 90 to 300 times (Table 88).

Table 88

Testing medium	Wt. loss, g/m² in 75 h							
	commercial iron		steel 20		steel 45		steel U8	
	untreated	Ti–Al–Si	untreated	Ti–Al–Si	untreated	Ti–Al–Si	untreated	Ti–Al–Si
3% NaCl	11.6	3	5.2	0	4.5	7	8.7	6
10% H_2SO_4	32	1567	76	1761	832	1232	1200	1503
30% HCl	592	3203	1766	2313	3543	372	1389	464
40% H_3PO_4	43	464	113	1602	1192	1372	1173	1628
10% HNO_3	6128	70	5748	27	6070	60	5720	18
50% CH_3COOH	42	120	39	44	50	—	42	0.9

4. ALUMINOZIRCOSILICONIZING*

Simultaneous diffusion coating of metals and alloys with a combination of Al–Zr–Si is carried out to improve their heat and corrosion resistance in various corrosive mediums.

Surface alloying is carried out in powder systems (metal powders) in containers provided with fusible seals [1, 28, 287] using powders of pure metals or their oxides (aluminothermic process).

Andreyeva et al. [287] have recommended the following composition of the active mixture as most suitable for diffusion-saturated aluminozircosiliconized coatings:

$$10\%\ Al+50\%\ Si+2\%\ Zr+36\%\ Al_2O_3+2\%\ NH_4Cl.$$

On the other hand, Tarasyuk et al. [28] have recommended active mixtures with moderate additions of silicon and zirconium:

$$50\%\ (10\text{–}15\%\ Si+10\text{–}15\%\ Zr+20\text{–}30\%\ Al)+45\%\ Al_2O_3+5\%\ NH_4Cl.$$

During the aluminothermic process of aluminozircosiliconizing, active atoms of zirconium and silicon are provided by their respective oxides.

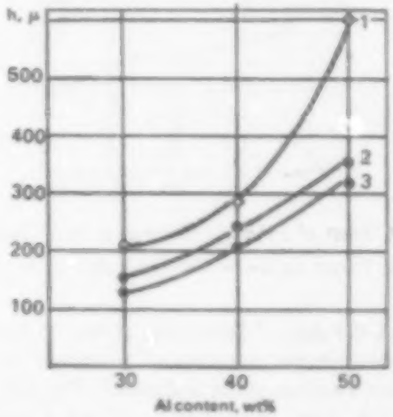

Fig. 128. Effect of aluminum content in active mixture on thickness of Al–Zr–Si coatings on (1) iron, (2) steel 45 and (3) steel U8:

Composition of mixture: $95\%\ \{40\%\ Al_2O_3+60\%\ [x\%\ Al+(100-x)\%\ (85\%\ ZrO_2+15\%\ SiO_2)]\}+5\%\ AlF_3$.

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*This terminology has been suggested by Tarasyuk et al. [28]. In our view it should be known as silicozircoaluminizing as the characteristics of the coating formed are similar to those of aluminized coatings.

The effect of the concentration of aluminum in an active mixture for zircosiliconizing on the formation of an Al–Zr–Si diffusion coating on plain carbon steels (keeping the concentrations of the oxides and activator (AlF_3) in the mixture constant) is shown in Fig. 128. Any increase in the aluminum content of the mixture is accompanied by an increase in the thickness of the diffusion layer. At concentrations of aluminum of 40% or more a preferred aluminizing takes place. Based on results of metallographic investigation on the effect of the technological parameters of the treatment on the thickness of the diffusion layer, the following composition of the active mixture is recommended as most suitable for carrying out aluminozircosiliconizing:

$$95\%\,[40\%\,Al_2O_3+60\%\,[30\text{–}40\%\,Al+70\text{–}60\%\,(85\%\,ZrO_2$$
$$+15\%\,SiO_2)]]+5\%\,AlF_3.$$

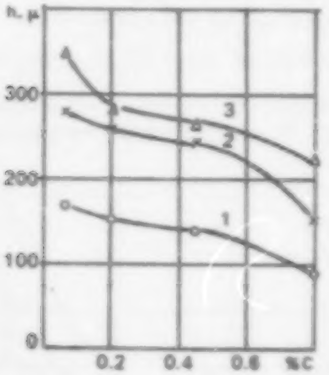

Fig. 129. Effect of carbon on thickness of Al–Zr–Si coatings: τ=8 h; Temperature—1—900°C; 2—1000°C; 3—1100°C.

Carbon hampers the rate of formation of the Al–Zr–Si layer (Fig. 129). The effect of temperature and duration of treatment on the thickness of a diffusion layer on plain carbon steels is shown in Fig. 130.

Aluminide, Fe_3Al_5, forms at the surface of aluminozircosiliconized coatings. Fe_2Al_5 is alloyed with zirconium and silicon and has a microhardness in the range of 715–680 kgf/mm². Precipitates of the silicide Zr_5Si_3 (H_{50}= 1100–1060) are observed in it. The zone of superlattices (FeAl and Fe_3Al), alloyed with aluminum, silicon and zirconium lies beneath the aluminides of iron. A disordered solid solution of aluminum, silicon and zirconium is found at the bottom of the diffusion layer in contact with the base metal. The zone of solid solutions has a variable microhardness, gradually decreasing in the direction of the center from 585 to 190 kgf/mm².

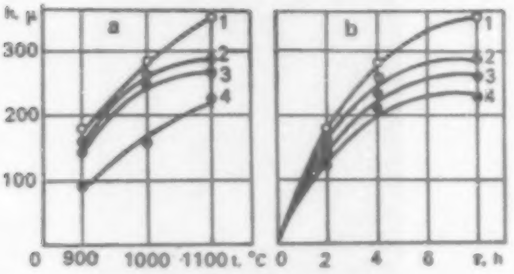

Fig. 130. Effect of temperature and duration of treatment on thickness of Al–Zr–Si diffusion coatings on (1) Armco iron, (2) steel 20, (3) steel 45 and (4) steel U8:

Composition of the active mixture: 95% {40% Al_2O_3 + 60% [n% Al + (100–n)% (85% ZrO_2 + 15% SiO_2)]} + 5% AlF_3.

$t = 1100$°C, $\tau = 4$ h.

Carbide, (Zr, Fe)C, with a microhardness in the range of 1590–1510 kgf/mm^2 is formed on the surface of plain carbon steels—steel 45 and steel U8. Beneath this layer lies an aluminide, Fe_2Al_5, alloyed with silicon and zirconium, with a microhardness in the range of 730–690 kgf/mm^2. Precipitates of zirconium silicide (Zr_5Si_3) (alloyed with iron and aluminum) and a microhardness of 1100–1080 kgf/mm^2 are observed in the Fe_2Al_5 phase. Beneath the aluminide layer lie ordered (FeAl, Fe_3Al) and disordered solid solutions of aluminum, silicon and zirconium in α-iron with a variable microhardness in the range of 585–190 kgf/mm^2. The concentrations of aluminum and silicon on the surface of aluminozircosiliconized steel 45 may reach 58.2 and 0.5%, respectively. The presence of zirconium in a diffusion layer has been established by qualitative spectroscopic analysis.

A typical structure of an aluminozircosiliconized coating on plain carbon steel is shown in Fig. 131.

Aluminozircosiliconized plain carbon steels have a high heat resistance which is, however, inferior to those of aluminized or aluminosiliconized specimens (Table 89).

Aluminozircosiliconizing improves the corrosion resistance of plain carbon steel in an aqueous solution of sodium chloride (quite effectively) and dilute acetic acid (to a lesser extent). Aluminozircosiliconizing fails to protect in mediums such as dilute hydrochloric, sulfuric, nitric and phosphoric acids (Table 90).

Simultaneous diffusion saturation of ZhS6K alloy with aluminum, silicon and zirconium has been carried out at 850°C for 6 h in powders of elements, their aggregate concentration being 50%. The remaining 50% of the active

Fig. 131. Microstructure of Al–Zr–Si coating on steel 45.

Table 89

Coating	Treatment parameters		Wt. gain, g/m² (1000°C, 26 h)			
	t, °C	τ, h	Commercial iron	steel 20	steel 45	steel U8
Untreated	—	—	1454	1310	1395	1100
Al–Zr–Si	1100	8	114	98	102	115
Al	1100	8	18	32	17	31
Al–Si	1100	8	15	16	16	17.5

mixture consisted of aluminum oxide (45%) and ammonium chloride (5%) [28]. Introduction of zirconium in this mixture has a similar effect as is seen in the case of chromium: the thickness as well as the microhardness decreases. In mixtures containing 30% or more of zirconium, the thickness of the diffusion layer does not exceed 15 μ. The diffusion coating is very brittle. Increasing the concentration of silicon in the mixture at a constant concentration of zirconium also leads to a reduction in thickness of the diffusion layer. However, in this case, its hardness increases.

Aluminozircosiliconized coatings are almost similar to aluminized coatings (for most of the mixture compositions) as far as their structures are concerned.

The exceptions are those coatings which are produced in active mixtures containing preponderant quantities of silicon. The distribution of the impregnating elements in the depth of the layer is shown in Fig. 118. For practical applications, it is recommended that active mixtures containing only small quantities of silicon and zirconium should be used. Tarasyuk et al. [28] have reported that aluminozircosiliconized ZhS6K alloy has a very high heat resistance.

Table 90

Corrosive medium	Treatment parameters t, °C, τ, h	Wt. loss, g/m^2 in 75 h			
		commercial iron	steel 20	steel 45	steel U8
3% NaCl	Untreated	11.6	5.2	4.5	8.7
	1100; 8	0.3	3	0.6	0.4
10% H_2SO_4	Untreated	32	76	832	1200
	1100; 8	656	1548	1543	1454
30% HCl	Untreated	592	1766	3543	1389
	1100; 8	1545	1893	2066	1114
40% H_3PO_4	Untreated	43	113	1192	1173
	1100; 8	712	1756	2320	2460
10% HNO_3	Untreated	6128	5748	6070	5720
	1100; 8	4770	4430	5500	280
50% CH_3COOH	Untreated	42	39	44	42
	1100; 8	17	50	10	10

Comparative data on the kinetics of oxidation of ZhS6K alloy with different types of protective coatings is given in Fig. 89. It can be seen from the figure that two- and three-component coatings have better protective quantities. Investigations were carried out at 1100°C for 200 h.

Information on some individual three-component coatings is also available in the literature.

Andreyeva et al. [287] have indicated that aluminozircosiliconized high-temperature creep-resistant alloys ZhS6K, EI-867 and EI-929 have a significantly higher heat resistance at 1100°C than those of aluminized and aluminosiliconized diffusion coating.

A high heat and corrosion resistance of aluminoborochromized diffusion coatings on ZhS6K alloy in an atmosphere of combustion products of sulfurous fuel, containing vapors of sea water, has been reported by Zemskov et al. [53, 304].

Chromotitanosiliconized coatings are employed by Messrs Thomson Woolridge for the protection of niobium and its alloys from oxidation. It has been observed that a multicomponent coating not only has a high heat resistance (it can withstand a temperature of 1375°C without damage for 90 h and 1260°C for 110–180 h), but also high thermal-shock resistance [351]. Similar data is also given in [345, 289].

The information on other three-component coatings is so limited that it would not be appropriate to examine it at this stage.

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